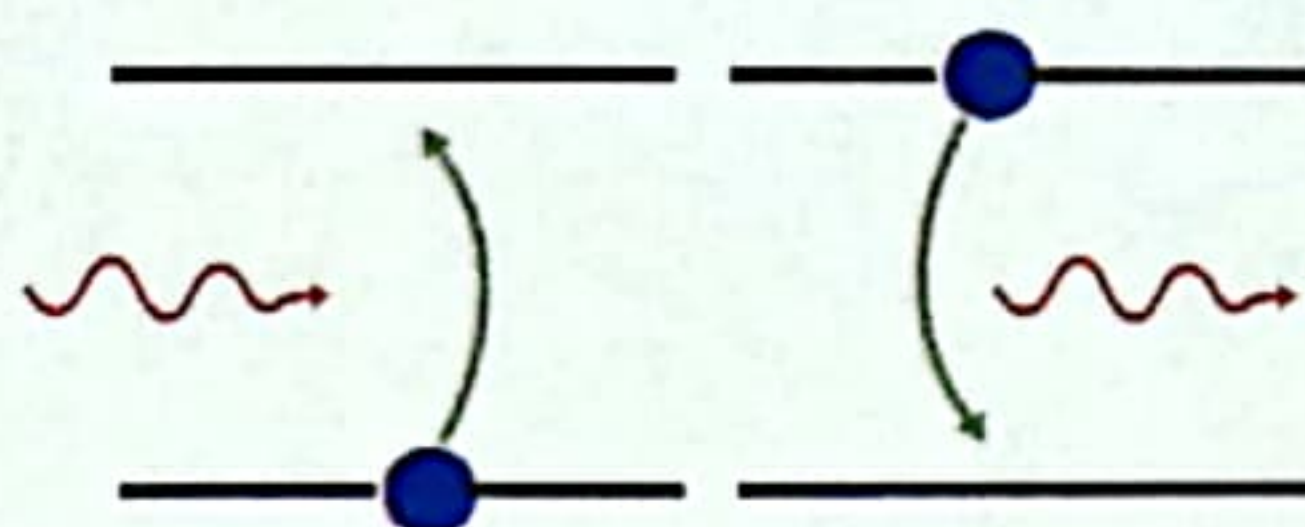




α

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Σ

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QUANTUM MECHANICS-II

2nd Edition

For Students of

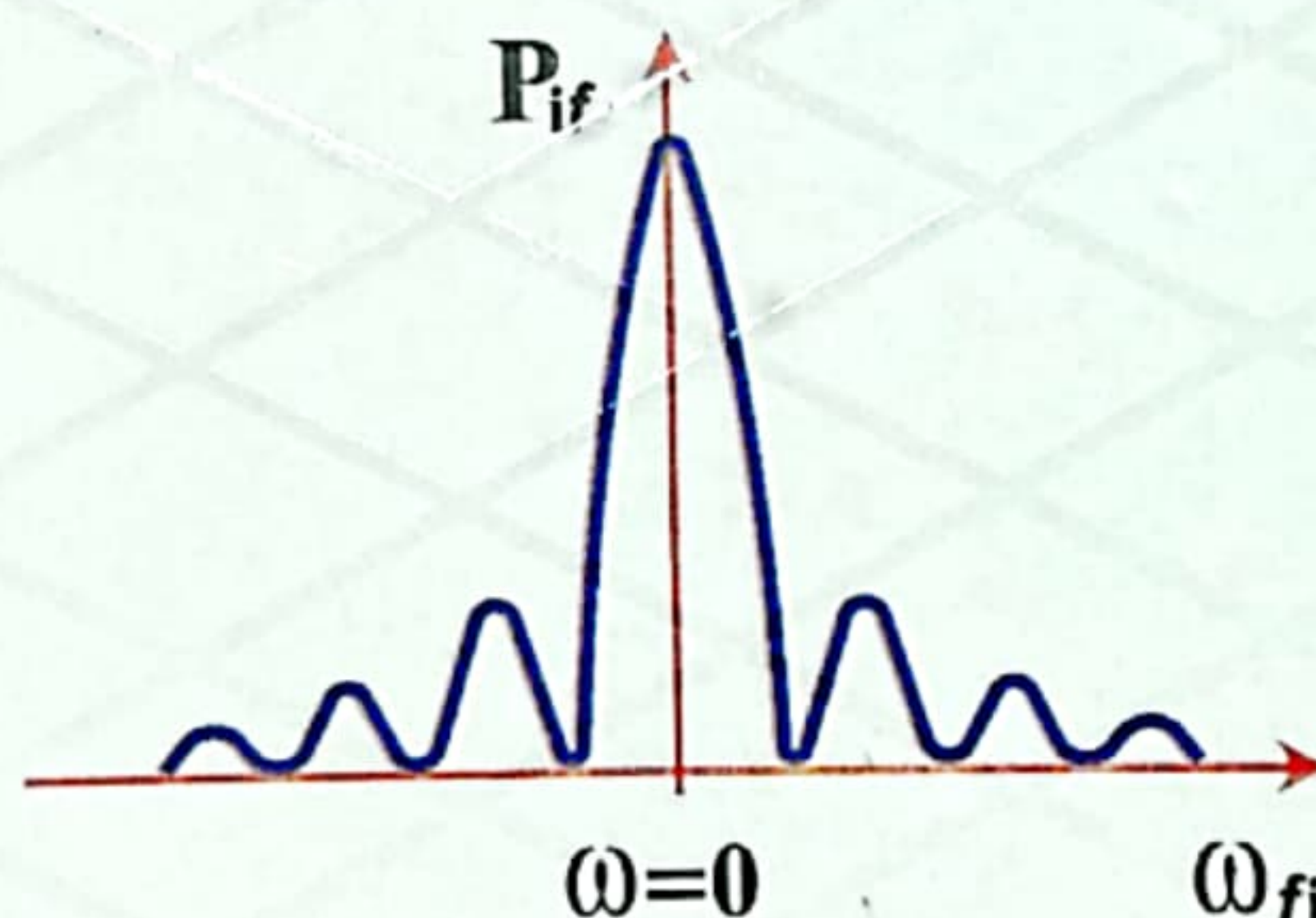
- > M.Sc Physics
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Salient Features

- > Essential questions & answers
- > Fully solved problems
- > Multiple choice Questions
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$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2$$

$$\hat{H} = \hat{H}_0 + \hat{H}_p$$



$$\frac{\partial}{\partial t} \rho + \nabla \cdot \mathbf{J} = 0$$

$$E^2 = p^2 c^2 + m_0^2 c^4$$

Dr. Syed Hamad Bukhari
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Hafiz Umer Farooq

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Chapter 1

Identical Particles

We want to examine systems with many particles. We shall focus on systems of identical particles and construct their wavefunctions. Two particles are identical if their all intrinsic properties (mass, spin, charge, magnetic moment, etc.) are same and therefore no experiment can distinguish them. Moreover, such particles (e.g. electron) can have different momentum, energy, angular momentum.

1.1 Schrödinger Wave Equation

The general form of the time independent Schrödinger wave equation for single particle is

$$\hat{H} \psi(r) = E \psi(r)$$
$$\left(\frac{P^2}{2m} + V(r) \right) \psi(r) = i\hbar \frac{\partial}{\partial t} \psi(r)$$

It can be extended to N-particles which is

$$\underbrace{\left[\sum_{i=1}^N \frac{P_i^2}{2m_i} + V(r_1, r_2, r_3, \dots, r_i, \dots, r_N) \right]}_{\text{Hamiltonian for N-particle}} \psi(r_1, r_2, r_3, \dots, r_i, \dots, r_N) = i\hbar \frac{\partial}{\partial t} \underbrace{\psi(r_1, r_2, r_3, \dots, r_i, \dots, r_N)}_{\text{Wavefunction for N-particles}}$$

where, r_i represent the coordinates (position, spin, etc) of i th particle. In quantum mechanics, the only measurements we can perform are those that specify the probability for

a certain particle to be located at r_1 , another at r_2 , and so on. But we can never make a distinction among particles, such as to which particle is which.

Probability

The state of a system of one spinless particles is $\psi(r)$. Generally, the probability density for one particle is

$$\psi(r) \psi^*(r) = |\psi|^2$$

The state of a system of N spinless particles is $\psi(r_1, r_2, r_3, \dots)$. Now, the probability density for N -particles is $|\psi(r_1, r_2, r_3, \dots)|^2$. The normalization condition of the state is

$$\int d^3r_1 \int d^3r_2 \int d^3r_3 \dots \int \psi(r_1, r_2, r_3, \dots, r_N) \psi^*(r_1, r_2, r_3, \dots, r_N) d^3r_N = 1$$

Bosons & Fermions

When we interchange position of i th and j th particles, the probability density remain same.

$$|\psi(r_1, r_2, r_3, \dots, r_i, \dots, r_j, \dots, r_N)|^2 = |\psi(r_1, r_2, r_3, \dots, r_j, \dots, r_i, \dots, r_N)|^2$$

Taking square root on both sides,

$$\psi(r_1, r_2, r_3, \dots, r_i, \dots, r_j, \dots, r_N) = \pm \psi(r_1, r_2, r_3, \dots, r_j, \dots, r_i, \dots, r_N)$$

Where

$$\psi(r_1, r_2, r_3, \dots, r_i, \dots, r_j, \dots, r_N) = \psi(r_1, r_2, r_3, \dots, r_j, \dots, r_i, \dots, r_N)$$

represents symmetric wavefunction related to spin of particles and positive sign corresponds to particles with integral spin ($S_i = 0\hbar, 1\hbar, 2\hbar, 3\hbar, \dots$) and

$$\psi(r_1, r_2, r_3, \dots, r_i, \dots, r_j, \dots, r_N) = -\psi(r_1, r_2, r_3, \dots, r_j, \dots, r_i, \dots, r_N)$$

represents antisymmetric wavefunction related to spin of particles and negative sign corresponds to particles with half-odd integral spin ($S_i = \frac{\hbar}{2}, \frac{3\hbar}{2}, \frac{5\hbar}{2}, \dots$)

Symmetrization Postulate

The symmetrization postulate states that, in nature, the states (wavefunction) of systems containing N identical particles are either totally symmetric or totally antisymmetric, under the interchange of any pair of particles and that states with mixed symmetry do not exist. All currently known particles obey the following empirical rules.

$$\psi(r_1, r_2, r_3, \dots, r_i \dots r_j \dots, r_N) = \pm \psi(r_1, r_2, r_3, \dots, r_j \dots r_i \dots, r_N)$$

Name	Wavefunction	Spin	Class
Symmetric	$\psi = +\psi$	$(S_i = 0, 1\hbar, 2\hbar, 3\hbar, \dots)$	Bosons
Anti-Symmetric	$\psi = -\psi$	$(S_i = \frac{\hbar}{2}, \frac{3\hbar}{2}, \frac{5\hbar}{2}, \dots)$	Fermions

1.2 Classes of Identical Particles

In quantum mechanics, identical particles are divided into two main classes, based on their spin

Bosons

All the particles with integral spin ($S = 0, 1\hbar, 2\hbar, 3\hbar, \dots$) are called Bosons. Such as π^- mesons ($S = 0$), photons ($S = 1\hbar$). They represent symmetric wavefunction.

Fermions

All the particles with half odd integral spin ($S = \frac{1\hbar}{2}, \frac{3\hbar}{2}, \frac{5\hbar}{2}, \dots$) are called fermions. Such as electrons ($S = \frac{1\hbar}{2}$), neutrons ($S = \frac{1\hbar}{2}$), protons ($S = \frac{1\hbar}{2}$) are fermions (see Figure 1.1). They represent anti-symmetric wavefunction.

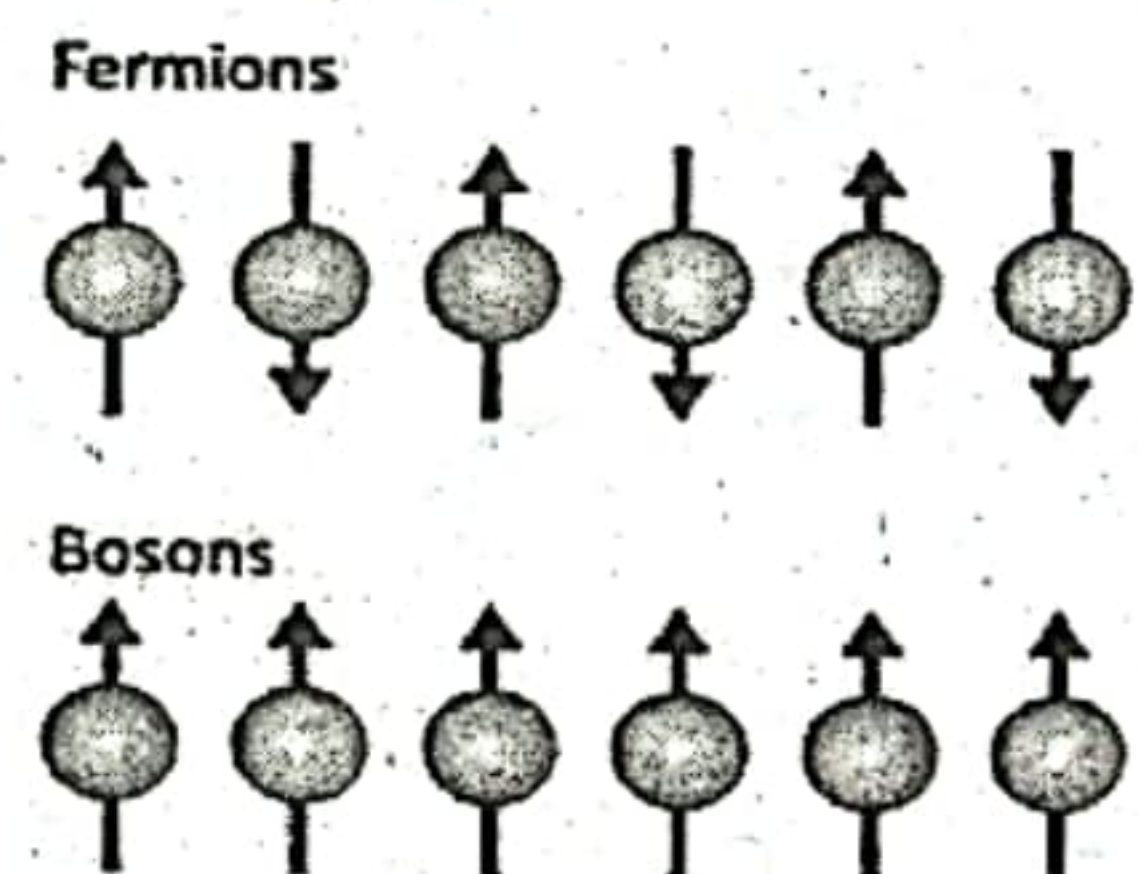


Fig. 1.1. Position of fermions and bosons condition.

Differentiate between Bosons and Fermions

Bosons

- ↪ They have integral spin. $S = 0, 1\hbar, 2\hbar, 3\hbar, \dots$
- ↪ They do not obey the Pauli Exclusion principle.
- ↪ They obey Bose-Einstein statistics.
- ↪ They are described by symmetric wave functions ($\psi = +\psi$).
- ↪ They create interaction between matter (e.g. energy).
- ↪ Examples: photon, gluon, graviton, W^+ , W^- , Z, etc.

Fermions

- ↪ They have half-odd integral spin. $S = \frac{1\hbar}{2}, \frac{3\hbar}{2}, \frac{5\hbar}{2}, \dots$
- ↪ They obey the Pauli Exclusion principle.
- ↪ They obey Fermi-Dirac statistics.
- ↪ They are described by anti-symmetric wave functions ($\psi = -\psi$).
- ↪ They make all the matter in the universe.
- ↪ Examples: electron, proton, neutron, quarks, neutrino, etc.

Composite Particles

Composite particle is composed of two or more identical elementary particles. For example, α -particles (${}^4\text{He}$), which consist of nuclei that are composed of two neutrons and two protons. Proton, neutron, pions etc are also composite particles, because protons and neutrons consist of three quarks and pions consist of two quarks.

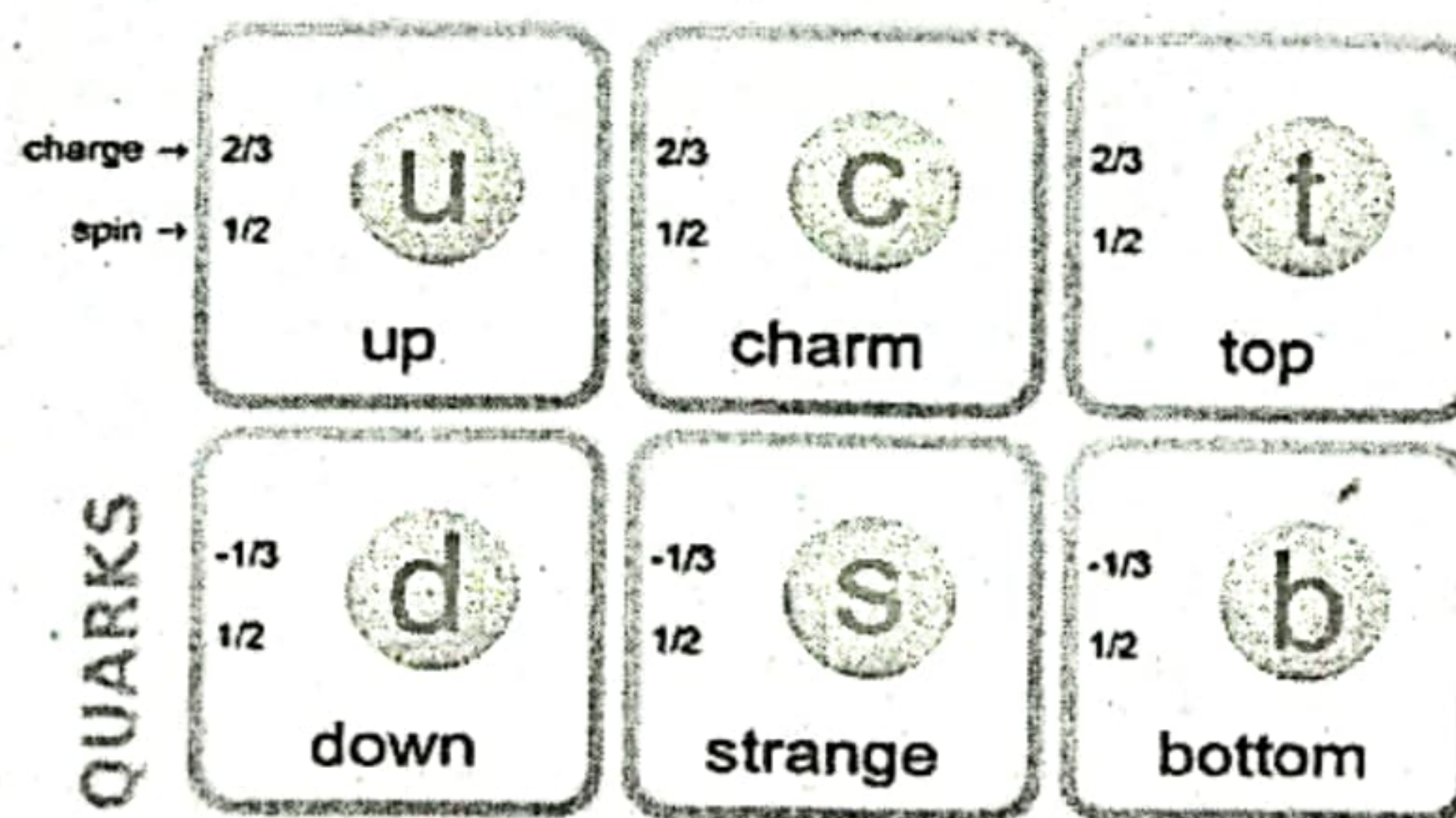


Fig. 1.2. All six types of quarks with spin and charge value.

The spin of each composite particle can be obtained by adding the spins of its constituents. If the total spin of the composite particle is half-odd-integer, this particle behaves like

a fermion. If, on the other hand, its resultant spin is integer, it behaves like a boson. In general, if the composite particle has an odd number of spin half constituents; then it is a fermion, otherwise it will be a boson.

For instance, nucleons are fermions because they consist of three quarks. Quarks are elementary spin particles (see Fig.1.2). For another example, let us consider the isotopes ^4He and ^3He of the helium atom: ^4He , an alpha particle, consists of four nucleons (two protons and two neutrons), while ^3He consists of three nucleons (one neutron and two protons). Because of resultant spin, ^4He is a boson and ^3He is a fermion. The hydrogen atom consists of two fermions (an electron and a proton), so it is a boson.

1.3 Systems of Identical Particles

Particles with same mass, spin and charge are called identical particles. Identical particles can be described into two categories

Distinguishable particles

In classical mechanics, when we have a system of identical particles, there is no problem to distinguish one from another.

- we can give a tag or number to particles.
- we can give a color to particles.
- we can easily follow their trajectory or path.
- Examples: Billard balls, football, etc.

In distinguishable Particles

In quantum mechanics, the identical nature of particles makes it impossible to define precisely the particle's trajectory and to distinguish one from another.

- we cannot give a tag or number to particles.
- we cannot give a color to particles.
- we cannot follow their trajectory or path.
- Examples: Electrons, protons, etc.

All electrons in anyone state are identical with respect to their mass, charge, spin and magnetic moment. This is because there is no such thing as this electron or that electron, as all electron are identical. So in quantum mechanics unlike classical mechanics, there is in principle no physical way of distinguishing, identical particles.

1.4 Exchange Operator ($\hat{P}_{ij}$) or Permutation Operator

We define an exchange operator $\hat{P}_{ij}$ as:

$$\hat{P}_{ij} \psi(r_1, r_2, r_3, \dots, r_i, \dots, r_j, \dots, r_N) = \psi(r_1, r_2, r_3, \dots, r_j, \dots, r_i, \dots, r_N)$$

Note that position of i th and the j th particles interchanged. i and j are arbitrary numbers. Since

$$\hat{P}_{ji} \psi(r_1, r_2, r_3, \dots, r_j, \dots, r_i, \dots, r_N) = \psi(r_1, r_2, r_3, \dots, r_i, \dots, r_j, \dots, r_N)$$

1.5 Exchange Degeneracy/invariant

Let us consider an atom with Z electrons, and $\vec{R}$ is representing the position of center of mass of the nucleus. The coulomb potential which results from electron-electron and electron-nucleus interactions, is invariant under the exchange of any pair of electrons. The Hamiltonian is also invariant (symmetric) under such permutations:

$$V(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_z) = \underbrace{-\sum_{i=1}^Z \frac{Ze^2}{|\vec{r}_i - \vec{R}|}}_{\text{electron-nucleus}} + \underbrace{\sum_{i>j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{\text{electron-electron}}$$

This symmetry also applies to the orbital, spin, and angular momenta of an atom. So, the N -particles of a system are said to be identical if the various observables of the system (such as Hamiltonian $\hat{H}$, the angular momenta and so on), are symmetrical when any two particles are interchanged by their positions¹. Hence, when the Hamiltonian $\hat{H}$ remains same under the exchange of particles then the wavefunctions corresponding to all possible electron exchanges have the same energy E . For example, transition of any

¹ If these operators were not remain same under particle interchange, the particles would be distinguishable.

Same Energy $\rightarrow$ Degeneracy

one electron from lower to higher orbit and another electron from higher to lower orbit. In such transitions, the energy of the system remains same. Thus eigen value of $\hat{H}$ is degenerate i.e. $\hat{H}\psi = E\psi$. This is known as **Exchange Degeneracy**.

1.6 A System of Identical Noninteracting Particles

Consider a system of N -noninteracting identical, indistinguishable particles. The wave function of each particle is $\psi_\alpha(1), \psi_\beta(2), \psi_\gamma(3)$, where 1, denotes the position coordinates (x_1, y_1, z_1) of particle 1, etc. while α , is the quantum state of particle 1 in the system etc. Thus the total wave function of N identical particles is

$$\psi_T = \psi(1, 2, 3 \dots N) = \psi_\alpha(1) \psi_\beta(2) \psi_\gamma(3) \dots \quad (1.1)$$

As they have different states so they are called non-interacting identical particles.

A system of two non-interacting identical particles

For simplicity, we assume that the system consists of only two identical non-interacting particles then Eq.(1.1) reduces to

$$\psi_{\alpha\beta}(1, 2) = \psi_\alpha(1) \psi_\beta(2) \quad (1.2)$$

States

$\psi_{\alpha\beta}(1, 2)$ means that particle 1 is in quantum state α and particle 2 is in quantum state β . If the position of two identical particles are interchanged then the new wave function of the system is given by

$$\psi_{\alpha\beta}(2, 1) = \psi_\alpha(2) \psi_\beta(1) \quad (1.3)$$

i.e. the particle 2, is in quantum state α , and particle 1, is in quantum state β . Always change position (1 & 2), not α & β . We know that if the particles are identical, the exchange of their positions would not change the probability density of the system i.e. (using Eq. 1.2 and 1.3),

$$|\psi_{\alpha\beta}(1, 2)|^2 = |\psi_{\alpha\beta}(2, 1)|^2 \quad (1.4)$$

The wave function can be symmetric or anti-symmetric $\psi_{\alpha\beta}(1, 2) = \pm \psi_{\alpha\beta}(2, 1)$. i.e. there is equal chance that the system of two identical particles is to be found in the state $\psi_{\alpha\beta}(1, 2)$ and the state $\psi_{\alpha\beta}(2, 1)$. We cannot write many particle wave function into the

Sub-Sub Shell

product of individual wave functions due to their indistinguishability. Thus the linear combination of these two wave functions should yield the eigen function of the system.

1.7 Symmetric and Antisymmetric Functions

Since, the wave function of system of identical particles is either totally symmetric or totally antisymmetric, it is appropriate to study the formalism of how to construct wave function that is totally symmetric or totally antisymmetric starting from asymmetric ($\alpha \neq \beta$) functions. For simplicity, consider first a system of two identical particles.

Symmetric Eigen Function (ψ_S)

$$\psi_S(1, 2) = \frac{1}{\sqrt{2}} [\psi_{\alpha\beta}(1, 2) + \psi_{\alpha\beta}(2, 1)] = \frac{1}{\sqrt{2!}} [\psi_{\alpha}(1) \psi_{\beta}(2) + \psi_{\alpha}(2) \psi_{\beta}(1)] \quad (1.5)$$

where $\frac{1}{\sqrt{2}}$ is normalization factor. For ($\alpha = \beta$, means same state), symmetric wave function $\psi_S(1, 2) \neq 0$. As the wavefunction exists ($\psi_S(1, 2) \neq 0$), this shows that any number of bosons can be in same quantum state.

Anti-Symmetric Eigen Function (ψ_A)

$$\psi_A(1, 2) = \frac{1}{\sqrt{2}} [\psi_{\alpha\beta}(1, 2) - \psi_{\alpha\beta}(2, 1)] = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_{\alpha}(1) & \psi_{\alpha}(2) \\ \psi_{\beta}(1) & \psi_{\beta}(2) \end{vmatrix} \quad (1.6)$$

Where $\frac{1}{\sqrt{2}}$ is normalization factor. Unlike the symmetric case, the anti-symmetric case for $\alpha = \beta$ same state is quite straightforward i.e. $\psi_A(1, 2) = 0$. As the wavefunction vanishes ($\psi_A = 0$), this shows that any number of fermions cannot exist in same quantum state. For N particles (Fermions) this determinant is called Slater determinant

$$\psi_A(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{\alpha}(1) & \psi_{\alpha}(2) & \dots & \psi_{\alpha}(N) \\ \psi_{\beta}(1) & \psi_{\beta}(2) & \dots & \psi_{\beta}(N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{\gamma}(1) & \psi_{\gamma}(2) & \dots & \psi_{\gamma}(N) \end{vmatrix} \quad (1.7)$$

1.8 Pauli Exclusion Principle

Pauli Exclusion Principle was first postulated in 1925 to explain the atomic order in periodic table by W. Pauli. It states that two electrons cannot occupy simultaneously the same quantum state having same spin on the same atom (see Figure 1.3). There can be only one electron occupying a state of quantum numbers (n, ℓ, m_ℓ, m_s) $\Psi_{n, \ell, m_\ell, m_s}(\vec{r}, \vec{S})$. This is known as **Pauli Exclusion Principle**. It means that all the electrons in any atom are in different states.

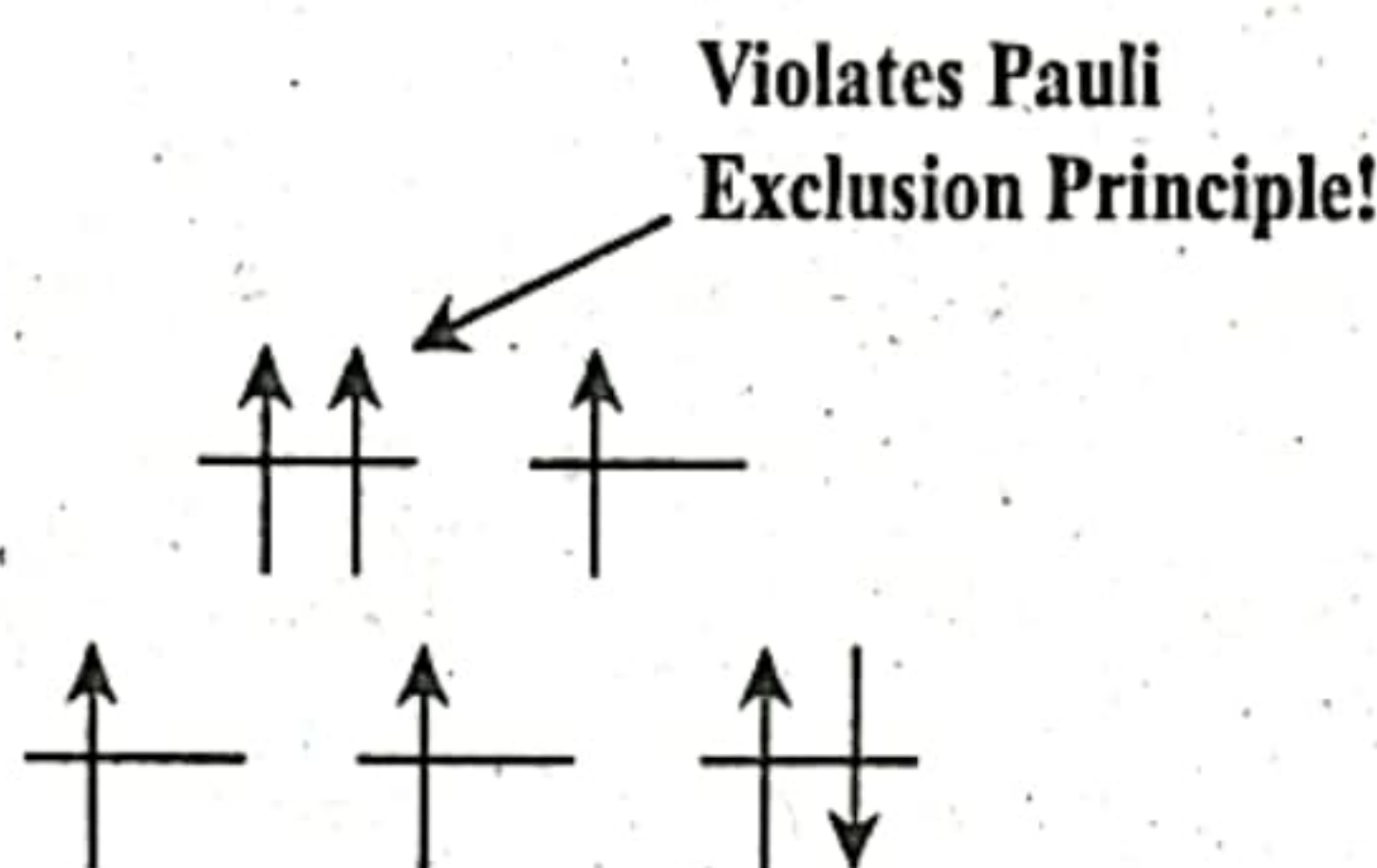


Fig. 1.3. Violation of Pauli principle

The Exclusion Principle and the Periodic Table

Explaining the periodic table is one of the most striking successes of the Schrodinger equation. When combined with the Pauli's exclusion principle, the equation gives the information about the structure of multi-electron atoms. The state of the hydrogen's electron, which moves in the spherically symmetric potential of nucleus is described by four quantum numbers n , ℓ , m_ℓ , and m_s .

$$\psi_{n\ell m_\ell m_s}(\vec{r}, \vec{S}) = \psi_{n\ell m_\ell}(\vec{r}) \chi_{m_s}$$

where $\chi_{m_s} = |\frac{1}{2}, \pm\frac{1}{2}\rangle$ is the spin's state. The electron's wave-function when the spin is ignored is given as:

$$\psi_{n\ell m_\ell m_s}(\vec{r}) = \psi_{n\ell m_\ell}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell m_\ell}(\theta, \phi)$$

The electronic states, as in hydrogen, are characterized by the four quantum numbers:

n = principal quantum number, $n=1,2,3,4,\dots$. It tells about shells.

ℓ = Azimuthal quantum number, $\ell=0,1,2,3,\dots,(n-1)$. It tells about sub-shells.

m_ℓ = magnetic quantum number, $m_\ell = (2\ell + 1)$. It tells about sub-sub-shells (orbitals).
 m_s = spin quantum number, $m_s = \pm 1/2$. It tells about the spin which is an intrinsic property.

As in hydrogen, individual electrons occupy single-particle states (orbitals), the states corresponding to the respective numerical values $\ell = 0, 1, 2, 3, 4, \dots$, are called $s, p, d, f, g, \dots$ states. How do electrons fill the various shells and sub-shells in an atom? If electrons were bosons, they would all group in the ground state $|nlm_\ell\rangle = |100\rangle$, we wouldn't then have the rich diversity of elements that exist in nature. But since electrons are identical fermions and satisfy the Pauli exclusion-principle, they cannot be in the same quantum state $|nlm_\ell m_s\rangle$.

Hence, each orbital $|nlm_\ell\rangle$ can occupy two electrons at most having spins, $m_s = \pm \frac{1}{2}$. Hence, each state nl can accommodate $2(2\ell + 1)$ electrons. Given below the state with electrons; $s = 2$ electrons; $p = 6$ electrons; $d = 10$ electrons; $f = 14$ electrons and so on. For an atom in the ground state, the electrons fill the orbitals in order of increasing energy. When all the orbitals in a major electronic shell are filled up, we get a closed shell; the next electron goes into the next major shell, and so on. By filling the atomic orbitals one after the other in order of increasing energy, one obtains all the elements of the periodic table.

Boson Condensation

There is no restriction on the number of bosons to occupy a single state. Instead of Pauli exclusion principle for fermions, bosons tend to condense all in the same state, the ground state. This is called boson condensation. Simply, gas into liquid is called condensation. For instance, all the particles of Liquid ^4He (a boson system) can occupy the same ground state. This phenomenon is known as Bose-Einstein condensation. Bose-Einstein condensate (BEC) is a state of matter of a dilute gas of bosons cooled to temperature very close to absolute zero (-273.15°C or 0 K).

Experiment

We can understand the Bose-Einstein condensation (BEC) by the following experiment. According to Bose and Einstein, atoms vibrate at room temperature (see Figure(1.4A)). However, if atoms are put into a chamber and reduce the temperature (very low), the vibration of atoms also reduces and atoms come closer (see Figure(1.4B)). They further

suggested that, if the temperature further slows down up to zero kelvin (0 K), which is the lowest possible temperature. These slow vibrating atoms are accumulating and transform themselves into wave like behavior (see Figure (1.4C)). It is basically transformation of matter into wave and it is like wave-particle duality. As the waves are formed with similar atoms, so these waves superimpose with each other (constructive interference) to form single wave (see Figure (1.4D)), also known as matter wave.

At the time, Einstein suggested this, 0 K is hard to achieve in laboratory. Then, in 2001, students of MIT, a university in USA have successfully performed the Bose-Einstein condensation with Rubidium atoms (^{86}Rb , a boson) at the temperature of 177 nK. On the verification of BEC, they also got Nobel prize for their experiments in 2001.

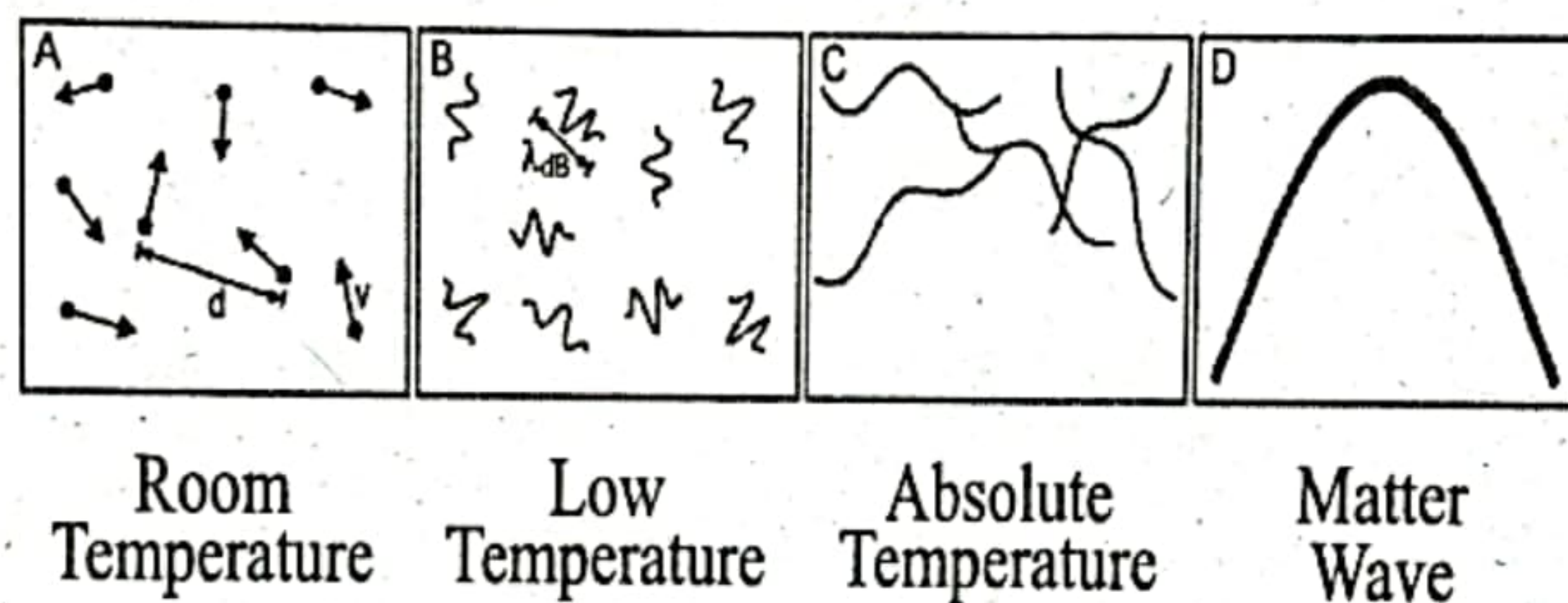


Fig. 1.4. Step-by-step schematic process of BEC.

1.9 Second Quantization

General form of quantum mechanics is denoted by first quantization. While quantum field theory is formulated in the language of second quantization. In second quantization, we discuss the **interaction between many particles** by introducing ladder operators. Thus, it is such a method in which particles may be created or destroyed. Second quantization formalism is based on knowledge of possible **quantum states** of a system and their occupation by **particles**.

For this purpose, time dependent abstract state vector for N-particles system is introduced. To connect first and second quantization, annihilation and creation operators for fermions and bosons are introduced.

Bosons System

Boson, which can share same quantum states, can be described by the state of bosons system as

$$S_+ |i_1, i_2, i_3, \dots, i\rangle |n_1, n_2, n_3, \dots\rangle = \frac{1}{\sqrt{n_1! n_2! \dots}}$$

where S_+ is creation/raising operators and $\frac{1}{\sqrt{n_1! n_2! \dots}}$ is the normalization factor.

n_1 is the number of particles in state i_1

n_2 is the number of particles in state i_2

If we add the occupation number

$$\sum_{i=1}^{\infty} n_i = N$$

where N is the total number of particles. Here, we are normalizing ($\langle\psi|\psi\rangle = 1$) the state vector $|n_1, n_2, n_3, \dots\rangle$. The result of the inner product is always a scalar, i.e.

$$\langle n_1, n_2, n_3, \dots | n_1, n_2, n_3, \dots \rangle = 1$$

Hence, the extended space is the sum of space with no particle (i.e. vacuum) $|0\rangle$, the space with one particle $|1\rangle$, the space with two particles $|2\rangle$, and so on. This sum of spaces is known as Fock Space. A Russian scientist Valdimir A. Fock (1898-1974) was first to introduce the concept

$$\text{Fock Space} = |0\rangle + |1\rangle + |2\rangle + \dots$$

Fermions System

Fermions, more than two do not share the same quantum state. We can describe the anti-symmetric state for fermions as

$$S_- |i_1, i_2, i_3, \dots, i_N\rangle = \frac{1}{\sqrt{n!}} \begin{vmatrix} |i_1\rangle_1 & |i_1\rangle_2 & \dots & |i_1\rangle_N \\ |i_2\rangle_1 & |i_2\rangle_2 & \dots & |i_2\rangle_N \\ \vdots & \vdots & & \vdots \\ |i_N\rangle_1 & |i_N\rangle_2 & \dots & |i_N\rangle_N \end{vmatrix}$$

This is the Slater determinant that only describes the anti-symmetric state. If any two rows are equal then the determinant becomes zero. This means that no two fermions can occupy the same state. This is known as Pauli exclusion principle. When all i_α are different, the anti-symmetric state is normalized. So, we characterize these states by specifying their occupation number

$$|n_1, n_2, n_3, \dots, \rangle$$

There are n_1 particles in state $|1\rangle$, and n_2 in state $|2\rangle$.

The state in which there is no particle i.e. $|0, 0, 0, \dots, \rangle$ are called Vacuum state. We can combine these states (vacuum state, single particle state, second particle state, and so on) to give a state space, the direct sum of these state spaces is known as Fock Space.

$$\text{Fock Space} = |0\rangle + |1\rangle + |2\rangle + \dots$$

1.10 Matrix Representation of Kets, Bras and Operators

Matrix representation of a Ket

Let us now represent the vector $|\psi\rangle$ within the context of discrete or countable, complete ($\sum_{n=1}^{\infty} |\phi_n\rangle \langle \phi_n| = I$) and orthonormal ($\langle \phi_n | \phi_m \rangle = \delta_{nm}$) basis $\{|\phi_n\rangle\}$

$$\{|\phi_n\rangle\} = |\phi_1\rangle, |\phi_2\rangle, |\phi_3\rangle, |\phi_4\rangle, \dots$$

$$|\psi\rangle = I |\psi\rangle = \left(\sum_{n=1}^{\infty} |\phi_n\rangle \langle \phi_n| \right) |\psi\rangle = \sum_{n=1}^{\infty} a_n |\phi_n\rangle$$

where the complex coefficients $a_n = \langle \phi_n | \psi \rangle$ represents the projection of $|\psi\rangle$ on to $|\phi_n\rangle$. So within the basis $\{|\phi_n\rangle\}$, the ket vector $|\psi\rangle$ is represented by the set of its components $a_1, a_2, a_3, \dots$ along $|\phi_1\rangle, |\phi_2\rangle, |\phi_3\rangle, \dots$ respectively. Hence, $|\psi\rangle$ can be represented by a column vector which has a countably infinite number of components:

$$|\psi\rangle \rightarrow \begin{pmatrix} \langle\phi_1|\psi\rangle \\ \langle\phi_2|\psi\rangle \\ \vdots \\ \langle\phi_n|\psi\rangle \\ \vdots \end{pmatrix} = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \\ \vdots \end{pmatrix}$$

Similarly quantum state vector $|\phi\rangle$ can be represented by a column vector as

$$|\phi\rangle \rightarrow \begin{pmatrix} \langle\phi_1|\phi\rangle \\ \langle\phi_2|\phi\rangle \\ \vdots \\ \langle\phi_n|\phi\rangle \\ \vdots \end{pmatrix} = \begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ b_n \\ \vdots \end{pmatrix}$$

Where coefficients are $b_n = \langle\phi_n|\phi\rangle$ as vector $|\phi\rangle$ can be expanded as $|\phi\rangle = \sum_{n=1}^{\infty} b_n |\phi_n\rangle$.

Matrix representation of a Bra

The bra vector $\langle\psi|$ (dual space of a ket vector $|\psi\rangle$) can be represented by a row vector as

$$\begin{aligned} \langle\psi| &\rightarrow (\langle\psi|\phi_1\rangle \langle\psi|\phi_2\rangle \cdots \langle\psi|\phi_n\rangle \cdots) \\ & (= \langle\phi_1|\psi\rangle^* \langle\phi_2|\psi\rangle^* \cdots \langle\phi_n|\psi\rangle^* \cdots) \\ & (= a_1^* a_2^* \cdots a_n^* \cdots) \end{aligned}$$

Where $a_1^* a_2^* a_3^* \cdots a_n^* \cdots$ are complex conjugate of $a_1, a_2, a_3, \cdots a_n \cdots$, respectively.

Bra-Ket as a Matrix Multiplication

The bra-ket $\langle \psi | \phi \rangle$ is a complex number and written as

$$\langle \psi | \phi \rangle (= a_1^* a_2^* \cdots a_n^* \cdots) \begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ b_n \\ \vdots \end{pmatrix}$$

$$\langle \psi | \phi \rangle (= a_1^* b_1 + a_2^* b_2 + \cdots a_n^* b_n \cdots)$$

$$\langle \psi | \phi \rangle = \sum_n a_n^* b_n$$

Where $b_n = \langle \phi_n | \phi \rangle$. We see that, within this representation, the matrices representing $|\psi\rangle$ and $\langle \psi|$ are Hermitian adjoints to each other.

1.11 Review Questions

- 1.1 Differentiate between bosons and fermions.
- 1.2 How can we differentiate the identical particle?
- 1.3 Why we cannot apply the exchange operator at one particle?
- 1.4 What is the effect of coulomb potential under permutation?
- 1.5 Can more than two fermions occupy the same state?
- 1.6 Why bosons cannot satisfy the Pauli's exclusion principle?
- 1.7 Justify ${}^4\text{He}$ is boson and ${}^3\text{He}$ is fermion.
- 1.8 Why atoms behave like waves at absolute temperature.
- 1.9 Differentiate between 1st and 2nd quantization.
- 1.10 What is Fock space?



1.12 Solved Problems

- 1.1. Consider a one-dimensional infinite square well of width 1cm with free electrons in it. If its Fermi energy is 2eV, what is the number of electrons inside the well?

Solution

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

where, $n = 1, 2, 3, \dots$ shows energy levels. Each level accommodate two electrons, one spin up and the other spin down. If the highest filled level is n , then the Fermi energy, $E_F = E_n$.

$$n^2 = \frac{2ma^2 E_F}{\pi^2 \hbar^2}$$

$$n^2 = \frac{(2 \times 1.6 \times 10^{-19} \text{ J}) \times 2 \times (9.1 \times 10^{-31} \text{ Kg}) (0.01 \text{ m})^2}{(3.14)^2 (1.05 \times 10^{-34} \text{ Js})^2}$$

$$n^2 = 5.3475 \times 10^{14}$$

$$n = 2.312 \times 10^7$$

The number of electrons (n) inside the well $= 4.62 \times 10^7$.



1.2. N non-interacting bosons are in an infinite potential well defined by $V(x) = 0$ for $0 < x < a$; $V(x) = \infty$ for $x < 0$ and for $x > a$. Find the ground state energy of the system. What would be the ground state energy if the particles are fermions?

Solution

The energy eigenvalue of a particle in the infinite square well is given by

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

As the particles are bosons, all the N -particles will be in the $n = 1$ state. Hence the total energy of system

$$E_{n_1, n_2, n_3 \dots n_N} = \frac{\pi^2 \hbar^2}{2ma^2} (1^2 + 1^2 + 1^2 \dots 1^2)$$

$$E = \frac{N \pi^2 \hbar^2}{2ma^2}$$

If the particles are fermions, a state can have only two of them, one spin up and the other spin down. Therefore, the lowest $\frac{N}{2}$ states will be filled. The total ground state energy will be

$$2\varepsilon_1, 2\varepsilon_2, 2\varepsilon_3 \dots \varepsilon_{\frac{N}{2}} = E^1 = \frac{\pi^2 \hbar^2}{2ma^2} [(1^2 + 1^2) + (2^2 + 2^2 +) \dots]$$

$$E^0 = \frac{N^3 \pi^2 \hbar^2}{24 ma^2}$$



1.3. Sixteen non-interacting electrons are confined in a potential $V(x) = \infty$ for $x < 0$ and $x > a$; $V(x) = 0$, for $0 < x < a$. (i) What is the energy of the least energetic electron in the ground state? (ii) What is the energy of the most energetic electron in the ground state? (iii) What is the Fermi energy E_F of the system?

Solution

(i) The least energetic electron in the ground state is given by

$$E_1 = \frac{\pi^2 \hbar^2}{2ma^2}$$

(ii) In the given potential, the energy eigenvalue is

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

As two electrons can go into each of the states $n = 1, 2, 3, \dots$, the highest filled level will have $n = 8$ and its energy will be

$$E_8 = \frac{8^2 \pi^2 \hbar^2}{2ma^2} = \frac{32\pi^2 \hbar^2}{ma^2}$$

(iii) The energy of the highest filled state is the Fermi energy E_F . Hence,

$$E_F = \frac{32\pi^2 \hbar^2}{ma^2}$$



1.4. Prove that it is impossible to construct a completely anti-symmetric spin function for three electrons.

Solution

Let a, b, c stands for three functions and 1,2,3 for three identical particles. In the function $a(1)b(2)c(3)$, particle 1 is in a , particle 2 is in b , and particle 3 is in c . Let us proceed without specifying that these functions correspond to space or spin functions. The third-order slater determinant for the case is

$$= \frac{1}{\sqrt{6}} \begin{vmatrix} a(1) & a(2) & a(3) \\ b(1) & b(2) & b(3) \\ c(1) & c(2) & c(3) \end{vmatrix}$$

This is completely anti-symmetrized as interchange of two spins amount to interchanging two columns of the determinant, which multiplies it by -1. Let us now specify the functions a, b, c as that due to electron spins. Let $a = \alpha, b = \beta, c = \beta$ in the above determinant. The determinant reduces to

$$= \frac{1}{\sqrt{6}} \begin{vmatrix} \alpha(1) & \alpha(2) & \alpha(3) \\ \beta(1) & \beta(2) & \beta(3) \\ \beta(1) & \beta(2) & \beta(3) \end{vmatrix}$$

As the second and third rows of the determinant are identical, its value is zero. In whatever way we select a, b, c , the two rows of the determinant will be equal. Therefore, we can not construct a completely anti-symmetric three-electron spin function.



1.5. The valence electron in the first excited state of an atom has the electronic configuration $3s^1, 3p^1$. (i) Under L-S coupling what value of L and S are possible? ii Write the spatial part of their wave-functions using the single particle functions $\psi_s(r)$ and $\psi_p(r)$.

Solution

i Electronic configuration $3s^1, 3p^1$. Hence

$$l_1 = 0, l_2 = 1$$

$$s_1 = \left(\frac{1}{2}\right), s_2 = \left(\frac{1}{2}\right)$$

$$L = 1, \quad S = 0, 1$$

ii Taking exchange degeneracy into account, the two possible space functions are

$$\psi_s(r_1)\psi_p(r_2) \quad \text{and} \quad \psi_s(r_2)\psi_p(r_1)$$

The symmetric combination

$$\psi_s = \frac{1}{\sqrt{2!}} [\psi_s(r_1) \psi_p(r_2) + \psi_s(r_2) \psi_p(r_1)]$$

Anti-symmetric combination

$$\psi_{as} = \frac{1}{\sqrt{2!}} [\psi_s(r_1) \psi_p(r_2) - \psi_s(r_2) \psi_p(r_1)]$$

where N_s and N_{as} are normalization constants.



1.13 Multiple Choice Questions

- 1: The wave functions of electron, proton and neutron are
 a) Symmetric b) Anti-symmetric c) mixed. d) None of these.
- 2: The wave functions of α particle, photon and deuteron are
 a) Symmetric b) Phonons c) Anti-symmetric d) None of these
- 3: $\psi_1(\vec{r}_1, \vec{r}_2(=)\vec{r}_1 - \vec{r}_2)^2$
 a) Symmetric b) Phonons c) Anti-symmetric d) None of these
- 4: Every single particle state can be occupied by at most one fermion is called
 a) Uncertainty principle b) Pauli principle c) Hund's rule d) Symmetry principle
- 5: The particles with integral spin, $S = 0, 1\hbar, 2\hbar, 3\hbar\dots$, are called
 a) Superconductor b) Neon c) Fermions d) Bosons
- 6: The exchange operator apply on
 a) single particle b) two particles c) Both d) None of these
- 7: A state of N fermions must be under every possible exchange operator:
 a) Anti-symmetric b) Symmetric c) Both d) None of these
- 8: The expression which describes the wave function of a multi-fermionic system that satisfies anti-symmetry conditions.
 a) Fock space b) Slater determinant c) Vaccum space d) None of these
- 9: Quarks are ... particles
 a) Fermions b) Bosons c) Elementary d) All
- 10: Quantum Field Theory describes the interaction among
 a) Fermions b) Bosons c) Elementary particles d) All

Answers

1	b	2	a	3	a	4	b	5	d
6	b	7	a	8	b	9	d	10	d

Chapter 2

Approximation Methods

An approximation is anything that is intentionally similar but not exactly equal to something else. In quantum mechanics, many problems cannot be solved exactly. Exact solutions of the Schrödinger equation exist only for a few ideal cases. It is often the case that the Hamiltonian of a system differs slightly from a Hamiltonian that is well studied and completely understood. To solve general problems, many approximation methods are developed. For the study of problems of stationary states corresponding to time independent Hamiltonian, we focus on three approximation methods.

1:-Perturbation Theory

2:-Variational Principle

3:-WKB Method

○ **Perturbation theory** given by Schrödinger in 1926, based on the assumption that the problem we wish to solve is only slightly different from a problem that can be solved exactly. Perturbation means disturbance produced in the system. When deviation between two problems is small, perturbation theory is good for calculation of these deviations. This difference is added as a correction to the energy and wavefunction of the exactly solved Hamiltonian. But for Hamiltonian, which cannot be reduced to an exactly solvable part plus a small deviation, we use variational method or WKB method.

○ **Variational principle** is useful in estimating the energy eigen values of ground state and first few excited states of the system. Here, we use some parameters to approxi-

mate/minimize the state which results the good estimation of eigen energies and eigen functions.

- **WKB method** is useful for finding the energy eigen values and wavefunctions of system for which the classical limit is valid. Unlike perturbation theory, the variational and WKB methods do not require the existence of a closely related Hamiltonian that can be solved exactly.

Depending upon the structure of $\hat{H}$, we can use any of the above three mentioned methods to find the approximate solutions of the eigen value,

$$\boxed{\hat{H} |\psi_n\rangle = E_n |\psi_n\rangle} \quad (2.1)$$

where, $\hat{H}$ is time independent Hamiltonian that does not have exact solutions.

2.1 Perturbation Theory

In quantum mechanics, when system is disturbed (by any means) then wavefunction and energy of the system will change. This sudden change in the system is called perturbation. Depending on the nature of problem perturbation theory is categorized into three classes

- ⇒ Time Independent Non-degenerate Perturbation Theory
- ⇒ Time Independent Degenerate Perturbation Theory
- ⇒ Time dependent Degenerate Perturbation Theory

In this Chapter, we study first two classes

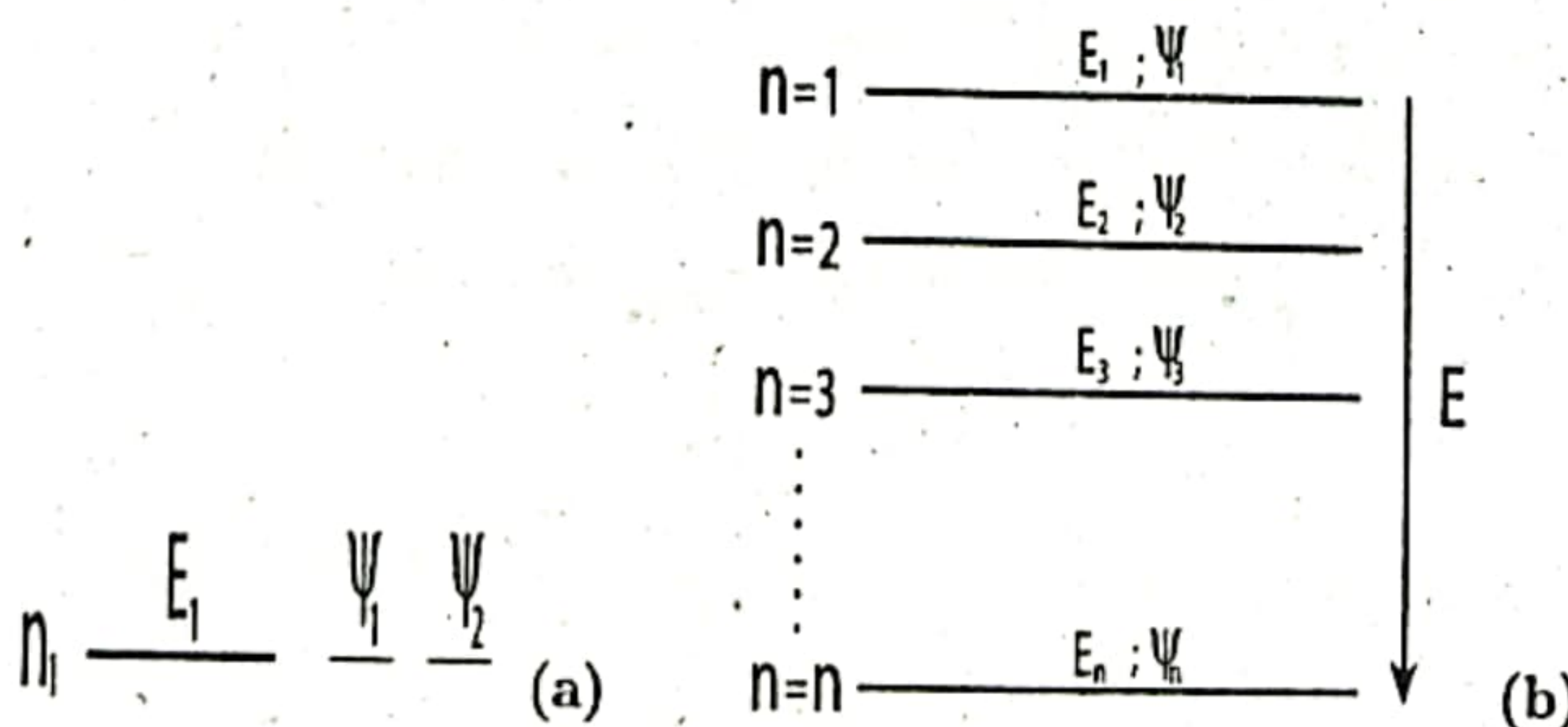


Fig. 2.1. Schematic picture (a) degenerate states (b) non-degenerate states.

Degenerate States

If two or more unperturbed states have same energy, they are said to be degenerate states

Non-degenerate States

If two or more unperturbed states have different energy in different states, they are said to be non-degenerate states as shown in Figure (2.1).

2.2 Time Independent Non-degenerate Perturbation

Let an unperturbed non-degenerate eigen state $|\psi_n^0\rangle$ of an unperturbed Hamiltonian $\hat{H}_0$ with energy E_n^0 . Then, the time independent Schrödinger wave equation for this unperturbed state will be

$$\hat{H}_0 |\psi_n^0\rangle = E_n^0 |\psi_n^0\rangle \quad (2.2)$$

Now, we perturb the system by small Hamiltonian $\hat{H}_P$. The time independent Hamiltonian ($\hat{H}$) after perturbation is

$$\hat{H} = \hat{H}_0 + \hat{H}_P \quad (2.3)$$

where, $\hat{H}_P$ is the perturbation very small compared to $\hat{H}_0$. ($\hat{H}_0$ can be solved exactly). Moreover, it is convenient to introduce a dimensionless real parameter λ which tells us about the strength of perturbation and its value is bound between 0 and 1 i.e. ($0 \leq \lambda \leq 1$). Thus, λ -dependent Hamiltonian $H(\lambda)$ that takes the form

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_P$$

Similarly, the total wavefunction after n th order perturbation is ¹,

$$|\psi_n\rangle = \lambda^0 |\psi_n^0\rangle + \lambda^1 |\psi_n^1\rangle + \lambda^2 |\psi_n^2\rangle + \dots \quad (2.4)$$

Also, the total energy after perturbation is (also see Fig. (2.2))

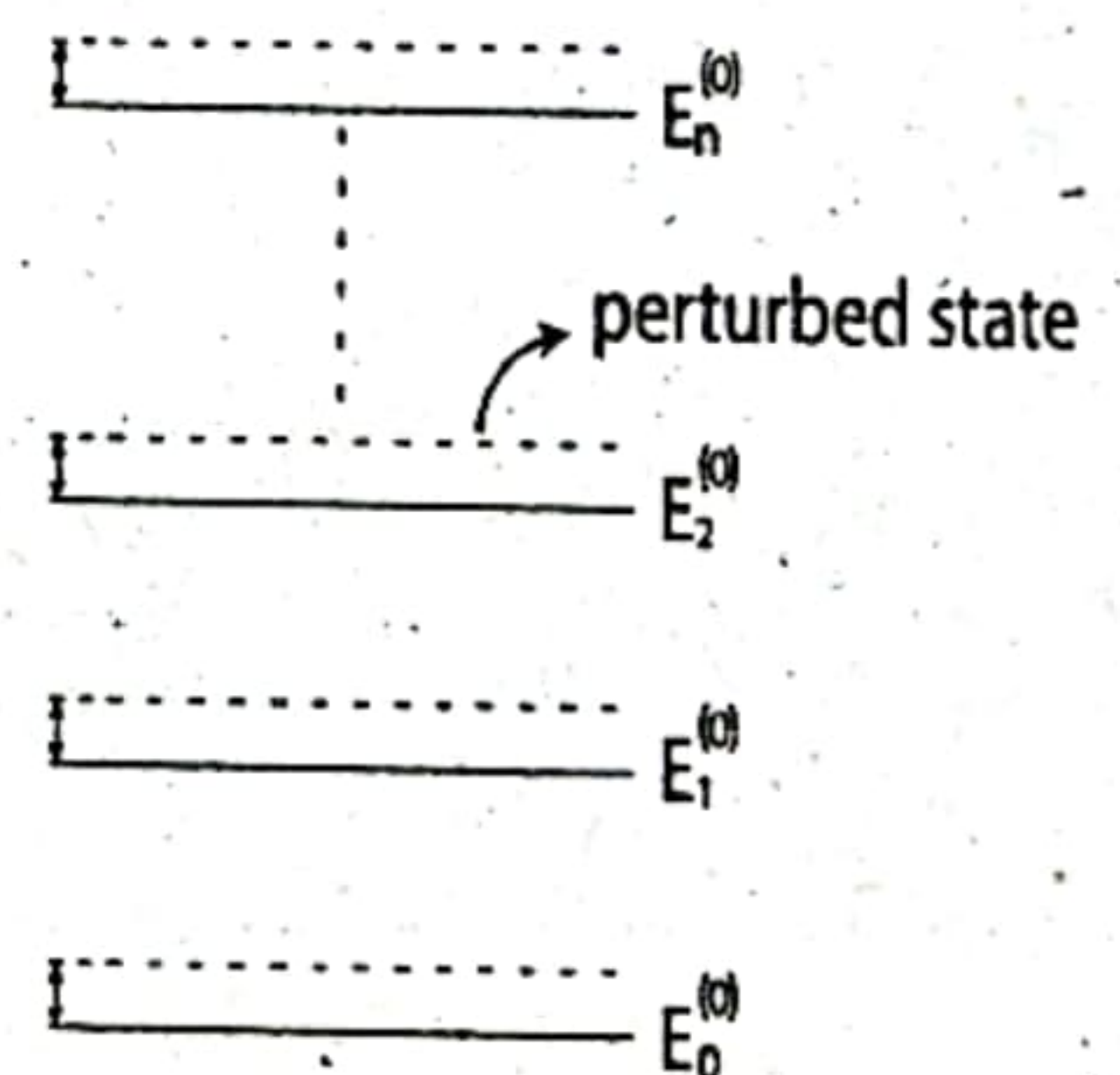


Fig. 2.2. Schematic picture of perturbed states

¹ Any perturbed quantity can be expanded in power series of λ .

$$E_n = \lambda^0 E_n^0 + \lambda^1 E_n^1 + \lambda^2 E_n^2 + \dots \quad (2.5)$$

Here, $|\psi_n^1\rangle$, $|\psi_n^2\rangle$ and E_n^1 , E_n^2 are the first and second order correction in wavefunction and energy, respectively. The series in Eq.(2.4) and Eq.(2.5) are not frequently convergent, we will take first few terms only.

Hence, the Schrödinger equation after perturbation is,

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle \quad (2.6)$$

Now, using the values of $|\psi_n\rangle$ and E_n in Eq.(2.6)

$$\begin{aligned} &(\hat{H}_0 + \lambda \hat{H}_P)(\lambda^0 |\psi_n^0\rangle + \lambda^1 |\psi_n^1\rangle + \lambda^2 |\psi_n^2\rangle + \dots) \\ &= (\lambda^0 E_n^0 + \lambda^1 E_n^1 + \lambda^2 E_n^2 + \dots)(\lambda^0 |\psi_n^0\rangle + \lambda^1 |\psi_n^1\rangle + \lambda^2 |\psi_n^2\rangle + \dots) \end{aligned}$$

$$\begin{aligned} &(\hat{H}_0 |\psi_n^0\rangle)\lambda^0 + (\hat{H}_0 |\psi_n^1\rangle + \hat{H}_P |\psi_n^0\rangle)\lambda^1 + (\hat{H}_0 |\psi_n^2\rangle + \hat{H}_P |\psi_n^1\rangle)\lambda^2 + \dots \\ &= (E_n^0 |\psi_n^0\rangle)\lambda^0 + (E_n^0 |\psi_n^1\rangle + E_n^1 |\psi_n^0\rangle)\lambda^1 + (E_n^0 |\psi_n^2\rangle + E_n^1 |\psi_n^1\rangle + E_n^2 |\psi_n^0\rangle)\lambda^2 + \dots \end{aligned}$$

Comparing the coefficients of $\lambda^0, \lambda^1, \lambda^2 \dots$, we get,

Zeroth order in λ

$$\hat{H}_0 |\psi_n^0\rangle = E_n^0 |\psi_n^0\rangle \quad (2.7)$$

First order in λ ,

$$\hat{H}_0 |\psi_n^1\rangle + \hat{H}_P |\psi_n^0\rangle = E_n^0 |\psi_n^1\rangle + E_n^1 |\psi_n^0\rangle \quad (2.8)$$

Second order in λ ,

$$\hat{H}_0 |\psi_n^2\rangle + \hat{H}_P |\psi_n^1\rangle = E_n^0 |\psi_n^2\rangle + E_n^1 |\psi_n^1\rangle + E_n^2 |\psi_n^0\rangle \quad (2.9)$$

Calculation of E_n^1

As perturbation is weak, so states $\langle\psi_n^0|$ and $|\psi_n\rangle$ overlap i.e. $\langle\psi_n^0|\psi_n\rangle = 1$. For first order correction, multiplying both sides of Eq.(2.8) by $\langle\psi_n^0|$

$$\begin{aligned} \langle \psi_n^0 | \hat{H}_0 | \psi_n^1 \rangle + \langle \psi_n^0 | \hat{H}_P | \psi_n^0 \rangle &= \langle \psi_n^0 | E_n^0 | \psi_n^1 \rangle + \langle \psi_n^0 | E_n^1 | \psi_n^0 \rangle \\ \underbrace{\langle \psi_n^0 | \hat{H}_0 | \psi_n^1 \rangle}_{= \langle \psi_n^0 | E_n^0} + \langle \psi_n^0 | \hat{H}_P | \psi_n^0 \rangle &= E_n^0 \underbrace{\langle \psi_n^0 | \psi_n^1 \rangle}_0 + E_n^1 \underbrace{\langle \psi_n^0 | \psi_n^0 \rangle}_1 \end{aligned}$$

Here, $\langle \psi_n^0 | \hat{H}_0 = \langle \psi_n^0 | E_n^0$

$$\begin{aligned} \langle \psi_n^0 | E_n^0 | \psi_n^1 \rangle + \langle \psi_n^0 | \hat{H}_P | \psi_n^0 \rangle &= E_n^1 \\ E_n^0 \underbrace{\langle \psi_n^0 | \psi_n^1 \rangle}_0 + \langle \psi_n^0 | \hat{H}_P | \psi_n^0 \rangle &= E_n^1 \end{aligned}$$

$$\boxed{E_n^1 = \langle \psi_n^0 | \hat{H}_P | \psi_n^0 \rangle} \quad (2.10)$$

This is the first order correction in energy i.e. E_n^1 . Where ψ_n^0 is unperturbed wavefunction and $\hat{H}_P$ is the perturbed Hamiltonian. Putting the value of E_n^1 in Eq.(2.5).

$$E_n = E_n^0 + \lambda \langle \psi_n^0 | \hat{H}_P | \psi_n^0 \rangle$$

Such inner product Eq. (2.10) can be written in the form of matrices, such that

$$\langle \psi_n^0 | \hat{H}_P | \psi_n^0 \rangle = \begin{pmatrix} \hat{H}_{P_{11}} & \hat{H}_{P_{12}} & \hat{H}_{P_{13}} & \cdots & \hat{H}_{P_{1n}} \\ \hat{H}_{P_{21}} & \hat{H}_{P_{22}} & \hat{H}_{P_{23}} & \cdots & \hat{H}_{P_{2n}} \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ \vdots & \vdots & \ddots & \ddots & \vdots \\ \hat{H}_{P_{n1}} & \hat{H}_{P_{n2}} & \hat{H}_{P_{n3}} & \cdots & \hat{H}_{P_{nn}} \end{pmatrix}$$

The diagonal values (i.e. $\hat{H}_{P_{11}}, \hat{H}_{P_{22}}, \dots, \hat{H}_{P_{nn}}$) of this matrix gives the eigen values of E_n^1 .

Calculation of $|\psi_n^1\rangle$

Let $|\psi_n^1\rangle$ can be expressed as a linear combination (i.e. sum of all terms) of a new unperturbed wave function ($|\psi_m^0\rangle$) as

$$|\psi_n^1\rangle = I |\psi_n^1\rangle = \left(\sum_{m \neq n} |\psi_m^0\rangle \langle \psi_m^0| \right) |\psi_n^1\rangle$$

$$|\psi_n^1\rangle = \sum_{m \neq n} \underbrace{\langle \psi_m^0 | \psi_n^1 \rangle}_{?} \underbrace{|\psi_m^0\rangle}_{\text{known}} \quad (2.11)$$

The coefficient $\langle \psi_m^0 | \psi_n^1 \rangle$ can be inferred from Eq(2.8). By multiplying both sides of Eq(2.8) by $\langle \psi_m^0 |$, we get

$$\begin{aligned} \langle \psi_m^0 | \hat{H}_0 | \psi_n^1 \rangle + \langle \psi_m^0 | \hat{H}_P | \psi_n^0 \rangle &= \langle \psi_m^0 | E_n^0 | \psi_n^1 \rangle + \langle \psi_m^0 | E_n^1 | \psi_n^0 \rangle \\ \underbrace{\langle \psi_m^0 | \hat{H}_0 | \psi_n^1 \rangle}_{= \langle \psi_m^0 | E_m^0 | \psi_n^1 \rangle} + \langle \psi_m^0 | \hat{H}_P | \psi_n^0 \rangle &= E_n^0 \langle \psi_m^0 | \psi_n^1 \rangle + E_n^1 \underbrace{\langle \psi_m^0 | \psi_n^0 \rangle}_{=0 \because m \neq n} \\ \langle \psi_m^0 | E_m^0 | \psi_n^1 \rangle + \langle \psi_m^0 | \hat{H}_P | \psi_n^0 \rangle &= E_n^0 \langle \psi_m^0 | \psi_n^1 \rangle \\ E_m^0 \langle \psi_m^0 | \psi_n^1 \rangle + \langle \psi_m^0 | \hat{H}_P | \psi_n^0 \rangle &= E_n^0 \langle \psi_m^0 | \psi_n^1 \rangle \\ \langle \psi_m^0 | \hat{H}_P | \psi_n^0 \rangle &= E_n^0 \langle \psi_m^0 | \psi_n^1 \rangle - E_m^0 \langle \psi_m^0 | \psi_n^1 \rangle \\ \langle \psi_m^0 | \hat{H}_P | \psi_n^0 \rangle &= (E_n^0 - E_m^0) \langle \psi_m^0 | \psi_n^1 \rangle \\ \frac{\langle \psi_m^0 | \hat{H}_P | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} &= \langle \psi_m^0 | \psi_n^1 \rangle \end{aligned}$$

So Eq.(2.11) becomes

$$|\psi_n^1\rangle = \sum_{m \neq n} \frac{\langle \psi_m^0 | \hat{H}_P | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} |\psi_m^0\rangle \quad (2.12)$$

This is the first order correction in wavefunction i.e. $|\psi_n^1\rangle$. Where ψ_m^0 and ψ_n^0 are the unperturbed wavefunctions with $\hat{H}_P$ as the perturbed Hamiltonian. By substitution, Eq. (2.4) becomes,

$$|\psi_n\rangle = |\psi_n^0\rangle + \lambda \sum_{m \neq n} \frac{\langle \psi_m^0 | \hat{H}_P | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} |\psi_m^0\rangle$$

Such inner product can be written in the form of matrices, such that

$$\langle \psi_m^0 | \hat{H}_P | \psi_n^0 \rangle = \begin{pmatrix} \hat{H}_{P_{11}} & \hat{H}_{P_{12}} & \hat{H}_{P_{13}} & \dots & \hat{H}_{P_{1n}} \\ \hat{H}_{P_{21}} & \hat{H}_{P_{22}} & \hat{H}_{P_{23}} & \dots & \hat{H}_{P_{2n}} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \hat{H}_{P_{m1}} & \hat{H}_{P_{m2}} & \hat{H}_{P_{m3}} & \dots & \hat{H}_{P_{mn}} \end{pmatrix}$$

The off-diagonal values (i.e. $m \neq n$) of this matrix gives the eigen values of $|\psi_n^1\rangle$.

Calculation of E_n^2

Multiplying Eq(2.9) by $\langle \psi_n^0 |$,

$$\langle \psi_n^0 | \hat{H}_0 | \psi_n^2 \rangle + \langle \psi_n^0 | \hat{H}_P | \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^2 \langle \psi_n^0 | \psi_n^0 \rangle$$

$$\text{As } \langle \psi_n^0 | \psi_n^1 \rangle = 0 \quad ; \quad \langle \psi_n^0 | \psi_n^2 \rangle = 0 \quad ; \quad \langle \psi_n^0 | \psi_n^0 \rangle = 1$$

$$E_n^0 (\langle \psi_n^0 | \psi_n^2 \rangle +) \langle \psi_n^0 | \hat{H}_P | \psi_n^1 \rangle = 0 + 0 + E_n^2$$

$$0 + \langle \psi_n^0 | \hat{H}_P | \psi_n^1 \rangle = E_n^2$$

$$\boxed{E_n^2 = \langle \psi_n^0 | \hat{H}_P | \psi_n^1 \rangle} \quad (2.13)$$

By putting the value of $|\psi_n^1\rangle$ from Eq(2.12) in above Eq.

$$E_n^2 = \sum_{m \neq n} \frac{\langle \psi_n^0 | \hat{H}_P | \psi_m^0 \rangle \langle \psi_m^0 | \hat{H}_P | \psi_n^0 \rangle}{(E_n^0 - E_m^0)}$$

$$= \sum_{m \neq n} \frac{\langle \psi_n^0 | \hat{H}_P | \psi_m^0 \rangle \langle \psi_m^0 | \hat{H}_P | \psi_n^0 \rangle}{(E_n^0 - E_m^0)}$$

$$= \sum_{m \neq n} - \frac{\langle \psi_m^0 | \hat{H}_P | \psi_n^0 \rangle \langle \psi_n^0 | \hat{H}_P | \psi_m^0 \rangle}{(E_n^0 - E_m^0)}$$

$$\boxed{E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | \hat{H}_P | \psi_n^0 \rangle|^2}{(E_n^0 - E_m^0)}} \quad (2.14)$$

For perturbation theory to work, the correction must be small i.e. $\frac{|\langle \psi_m^0 | \hat{H}_P | \psi_n^0 \rangle|^2}{(E_n^0 - E_m^0)} \ll 1$.

2.3 Time Independent Degenerate perturbation

We apply perturbation theory to determine the energy spectrum and the states of a system whose unperturbed Hamiltonian $\hat{H}_0$ is degenerate.

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$$

As $\hat{H} = \hat{H}_0 + \hat{H}_P$

$$(\hat{H}_0 + \hat{H}_P)|\psi_n\rangle = E_n|\psi_n\rangle \quad (2.15)$$

If, for instance, the level of energy E_n^0 is f -fold degenerate. (i.e. There exists a set of f different eigen states $|\psi_{n\alpha}^0\rangle$, where $\alpha = 1, 2, 3, 4, \dots, f$ that correspond to the same eigen energy E_n^0 .)

$$\hat{H}_0 |\psi_{n\alpha}^0\rangle = E_n^0 |\psi_{n\alpha}^0\rangle, \quad (2.16)$$

where α stands for one or more quantum numbers. The energy eigen values E_n^0 are independent of α . In the zeroth order (i.e. λ^0) approximation we can write the eigen function $|\psi_n\rangle$ as a linear combination in terms of $|\psi_{n\alpha}^0\rangle$ unperturbed states.

$$|\psi_n\rangle = \sum_{\alpha=1}^f a_{\alpha} |\psi_{n\alpha}^0\rangle \quad (2.17)$$

Considering the states $|\psi_{n\alpha}^0\rangle$ to be orthonormal with respect to label i.e. $\langle \psi_{n\alpha}^0 | \psi_{n\beta}^0 \rangle = \delta_{\alpha\beta}$ and $|\psi_n\rangle$ to be normalized, $\langle \psi_n | \psi_n \rangle = 1$. Taking complex conjugate of Eq.(2.17)

$$\begin{aligned} (|\psi_n\rangle)^* &= \left(\sum_{\alpha=1}^f a_{\alpha} |\psi_{n\alpha}^0\rangle \right)^* \\ \langle \psi_n| &= \sum_{\alpha=1}^f a_{\alpha}^* \langle \psi_{n\alpha}^0| \end{aligned} \quad (2.18)$$

By using values of $\langle \psi_n|$ from Eq(2.18) and $|\psi_n\rangle$ from Eq(2.17), we have

$$\begin{aligned}\langle \psi_n | \psi_n \rangle &= 1 \\ \sum_{\alpha=1}^f \langle \psi_{n_\alpha}^0 | a_\alpha^* a_\alpha | \psi_{n_\alpha}^0 \rangle &= 1 \\ \sum_{\alpha=1}^f |a_\alpha|^2 \langle \psi_{n_\alpha}^0 | \psi_{n_\alpha}^0 \rangle &= 1 \\ \sum_{\alpha=1}^f |a_\alpha|^2 &= 1\end{aligned}$$

We are going to determine the coefficients and the first order corrections (E_n^1) to the energy. Putting the value of $|\psi_n\rangle$ from Eq(2.17) in Eq. (2.15), we get

$$\begin{aligned}\sum_{\alpha=1}^f (\hat{H}_o + \hat{H}_p) a_\alpha | \psi_{n_\alpha}^0 \rangle &= E_n \sum_{\alpha=1}^f a_\alpha | \psi_{n_\alpha}^0 \rangle \\ \sum_{\alpha=1}^f (\hat{H}_o | \psi_{n_\alpha}^0 \rangle + \hat{H}_p | \psi_{n_\alpha}^0 \rangle) a_\alpha &= E_n \sum_{\alpha=1}^f a_\alpha | \psi_{n_\alpha}^0 \rangle\end{aligned}$$

The first term, $\hat{H}_o | \psi_{n_\alpha}^0 \rangle = E_n^0 | \psi_{n_\alpha}^0 \rangle$

$$\sum_{\alpha=1}^f (E_n^0 | \psi_{n_\alpha}^0 \rangle + \hat{H}_p | \psi_{n_\alpha}^0 \rangle) a_\alpha = E_n \sum_{\alpha=1}^f a_\alpha | \psi_{n_\alpha}^0 \rangle$$

Multiplying both sides of above by $\langle \psi_{n_\beta}^0 |$

$$\begin{aligned}\sum_{\alpha=1}^f (E_n^0 \langle \psi_{n_\beta}^0 | \psi_{n_\alpha}^0 \rangle + \langle \psi_{n_\beta}^0 | \hat{H}_p | \psi_{n_\alpha}^0 \rangle) a_\alpha &= E_n \sum_{\alpha=1}^f a_\alpha \langle \psi_{n_\beta}^0 | \psi_{n_\alpha}^0 \rangle \\ \sum_{\alpha=1}^f a_\alpha (E_n^0 \delta_{\alpha\beta} + \langle \psi_{n_\beta}^0 | \hat{H}_p | \psi_{n_\alpha}^0 \rangle) &= E_n \sum_{\alpha=1}^f a_\alpha \delta_{\alpha\beta} \\ \sum_{\alpha=1}^f E_n^0 a_\alpha \delta_{\alpha\beta} + \sum_{\alpha=1}^f a_\alpha \langle \psi_{n_\beta}^0 | \hat{H}_p | \psi_{n_\alpha}^0 \rangle &= E_n \sum_{\alpha=1}^f a_\alpha \delta_{\alpha\beta} \\ \sum_{\alpha=1}^f a_\alpha \langle \psi_{n_\beta}^0 | \hat{H}_p | \psi_{n_\alpha}^0 \rangle &= \sum_{\alpha=1}^f (E_n - E_n^0) a_\alpha \delta_{\alpha\beta}\end{aligned}$$

By putting $\langle \psi_{n_\beta}^0 | \hat{H}_p | \psi_{n_\alpha}^0 \rangle = \hat{H}_{p\beta\alpha}$

$$\sum_{\alpha=1}^f a_{\alpha} \hat{H}_{p\beta\alpha} = \sum_{\alpha=1}^f (E_n - E_n^0) a_{\alpha} \delta_{\alpha\beta}$$

We know that

$$E_n = E_n^0 + E_n^1 \quad (2.19)$$

$$E_n - E_n^0 = E_n^1$$

$$\sum_{\alpha=1}^f a_{\alpha} \hat{H}_{p\beta\alpha} = \sum_{\alpha=1}^f E_n^1 a_{\alpha} \delta_{\alpha\beta}$$

$$\sum_{\alpha=1}^f a_{\alpha} \hat{H}_{p\beta\alpha} - \sum_{\alpha=1}^f E_n^1 a_{\alpha} \delta_{\alpha\beta} = 0,$$

$$\sum_{\alpha=1}^f \left(\hat{H}_{p\beta\alpha} - E_n^1 \delta_{\alpha\beta} \right) a_{\alpha} = 0, \quad (2.20)$$

where, $(\beta = 1, 2, 3, \dots, f)$. This is a system of f homogeneous linear equations for the coefficients a_{α} . These coefficients are non vanishing only when the determinant.

$$|\hat{H}_{p\beta\alpha} - E_n^1 \delta_{\alpha\beta}| = 0$$

$$\begin{vmatrix} (\hat{H}_{p11} - E_n^1) & \hat{H}_{p12} & \hat{H}_{p13} & \dots & \hat{H}_{p1f} \\ \hat{H}_{p21} & (\hat{H}_{p22} - E_n^1) & \hat{H}_{p23} & \dots & \hat{H}_{p2f} \\ \hat{H}_{p31} & \hat{H}_{p32} & (\hat{H}_{p33} - E_n^1) & \dots & \hat{H}_{p3f} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \hat{H}_{pf1} & \hat{H}_{pf2} & \hat{H}_{pf3} & \dots & (\hat{H}_{pff} - E_n^1) \end{vmatrix} = 0 \quad (2.21)$$

(We have used if $\alpha \neq \beta$, $\delta_{\alpha\beta} = 0$). As operator is changing, so E_n^1 is also changing thus there is no degeneracy. This is an f^{th} degree equation in E_n^1 and in general it has f different real roots, $E_{n\alpha}^1$. These roots are the first order correction to the eigen values, $E_{n\alpha}$, of $\hat{H}$. We can find coefficients (a_{α}) by putting these roots in Eq. (2.20) and solve the resulting expression. The roots of Eq.(2.21) are in general different. In this case the eigen values are not degenerate, hence the f -fold degenerate level E_n^0 of the unperturbed problem is split into f different levels $E_{n\alpha}$.

2.3. TIME INDEPENDENT DEGENERATE PERTURBATION

$$E_{n\alpha} = E_n^0 + E_{n\alpha}^1, \quad \alpha = 1, 2, \dots, f$$

In this way the perturbation lifts the degeneracy. The lifting of degeneracy may be either total or partial, depending on whether all the roots of Eq.(2.21), or few are different. To determine the eigen states to zeroth order for an f fold degenerate level from perturbation theory, we proceed as follows.

1. For each f fold degenerate level, determine the $f \times f$ matrix of the perturbation $\hat{H}_P$

$$\hat{H}_P = \begin{pmatrix} \hat{H}_{p11} & \hat{H}_{p12} & \dots & \hat{H}_{p1f} \\ \hat{H}_{p21} & \hat{H}_{p22} & \dots & \hat{H}_{p2f} \\ \vdots & \vdots & \ddots & \vdots \\ \hat{H}_{pf1} & \hat{H}_{pf2} & \dots & \hat{H}_{pff} \end{pmatrix}$$

where $\hat{H}_{p\alpha\beta} = \langle \psi_{n\alpha}^0 | \hat{H}_P | \psi_{n\beta}^0 \rangle$.

2. Diagonalized the matrix $\hat{H}_P$ and find f eigen values: $E_{n\alpha}^1$, ($\alpha = 1, 2, \dots, f$) and their corresponding eigen vectors.

$$\alpha_\beta = \begin{pmatrix} a_{\alpha 1} \\ a_{\alpha 2} \\ \vdots \\ a_{\alpha f} \end{pmatrix}$$

where ($\beta = 1, 2, \dots, f$.)

Finally, the energy eigen values are given to first order by,

$$\boxed{E_{n\alpha} = E_n^0 + E_{n\alpha}^1} \quad (2.22)$$

And the corresponding eigen vectors are given to zeroth order by

$$\boxed{|\psi_{n\alpha}\rangle = \sum_{\beta=1}^f a_{\alpha\beta} |\psi_{n\beta}^0\rangle} \quad (2.23)$$

2.4 Variational Principle or Rayleigh Ritz Method

The variational method is useful for determining eigen energies and eigen states of a system whose Hamiltonian is known but it cannot be solved exactly or by a perturbative treatment. It is particularly useful for determining the ground state of a quantum system. For a system described by Hamiltonian $\hat{H}$, the ground state energy is calculated by variational principle without solving the time independent Schrödinger equation. According to this principle, the ground state energy (E_g) of the system is the expectation value of Hamiltonian $\hat{H}$ in normalized state $|\psi\rangle$.

$$E_g \leq \langle \psi | \hat{H} | \psi \rangle = \langle \hat{H} \rangle$$

In ground state, energy is E_g but if $|\psi\rangle$ is in excited state, then $\langle \hat{H} \rangle$ exceeds E_g .

Proof

The trial wavefunction $|\psi\rangle$ is the linear combination of different exact eigen states of $\hat{H}$

$$|\psi\rangle = \sum_n c_n |\phi_n\rangle \quad (2.24)$$

Taking complex conjugate of Eq(2.24)

$$\langle \psi | = \sum_n c_n^* \langle \phi_n | \quad (2.25)$$

As, the given wavefunction is normalized, so condition of normalization will be satisfied i.e. $\langle \psi | \psi \rangle = 1$.

$$\begin{aligned} \langle \psi | \psi \rangle &= 1 \\ \sum_n \sum_n c_n^* c_n \langle \phi_n | \phi_n \rangle &= 1 \\ \sum_n c_n^* c_n (1) &= 1 \\ \sum_n |c_n|^2 &= 1 \end{aligned}$$

Now, the expectation value of Hamiltonian is $\hat{H}$

$$\begin{aligned}
\langle \hat{H} \rangle &= \langle \psi | \hat{H} | \psi \rangle \\
\langle \hat{H} \rangle &= \sum_n \sum_n c_n^* c_n \langle \phi_n | \hat{H} | \phi_n \rangle \\
\langle \hat{H} \rangle &= \sum_n c_n^* c_n E_n \langle \phi_n | \phi_n \rangle \\
\langle \hat{H} \rangle &= \sum_n c_n^* c_n E_n (1) \\
\langle \hat{H} \rangle &= \sum_n |c_n|^2 E_n \\
\langle \hat{H} \rangle &= (1) E_n
\end{aligned}$$

Hence, we have

$$\langle \hat{H} \rangle = E_n \quad (2.26)$$

Now, as the ground state is the smallest eigen value

$$\boxed{E_g \leq \langle \hat{H} \rangle} = E_n$$

This is the required result. In general, to calculate the ground state and ground state energy, make an educated guess of a trial function that contains all the physical properties of the ground state (symmetries, smoothness etc) in terms of adjustable parameters $\alpha_1, \alpha_2, \alpha_3, \dots$ (i.e. $|\psi\rangle = |\psi(\alpha_1, \alpha_2, \alpha_3, \dots)\rangle$). Then searching for the minimum value of $\langle H \rangle$ by varying the adjustable parameters α_i , so one get the closest estimated possible eigen state and energy for the selected trial function. For example, for calculating the ground state of Hydrogen atom, the best trial function is $\psi = e^{-\alpha x}$, where α is the variable parameter.

2.5 Wentzel Kramers Brillouin (WKB) Method

WKB method is a technique for obtaining approximate solutions to time independent Schrödinger equation. It is particularly useful in finding the energy eigen values and wave functions of system for which classical limit is valid i.e. by WKB method we can calculate bound state energies and tunneling rates through potential barrier. In WKB, we treat the system with slowly varying potentials that is potential which remains almost constant over a region of the order of de-Broglie wavelength ($\lambda = h/P$). In classical systems ($E > V$),

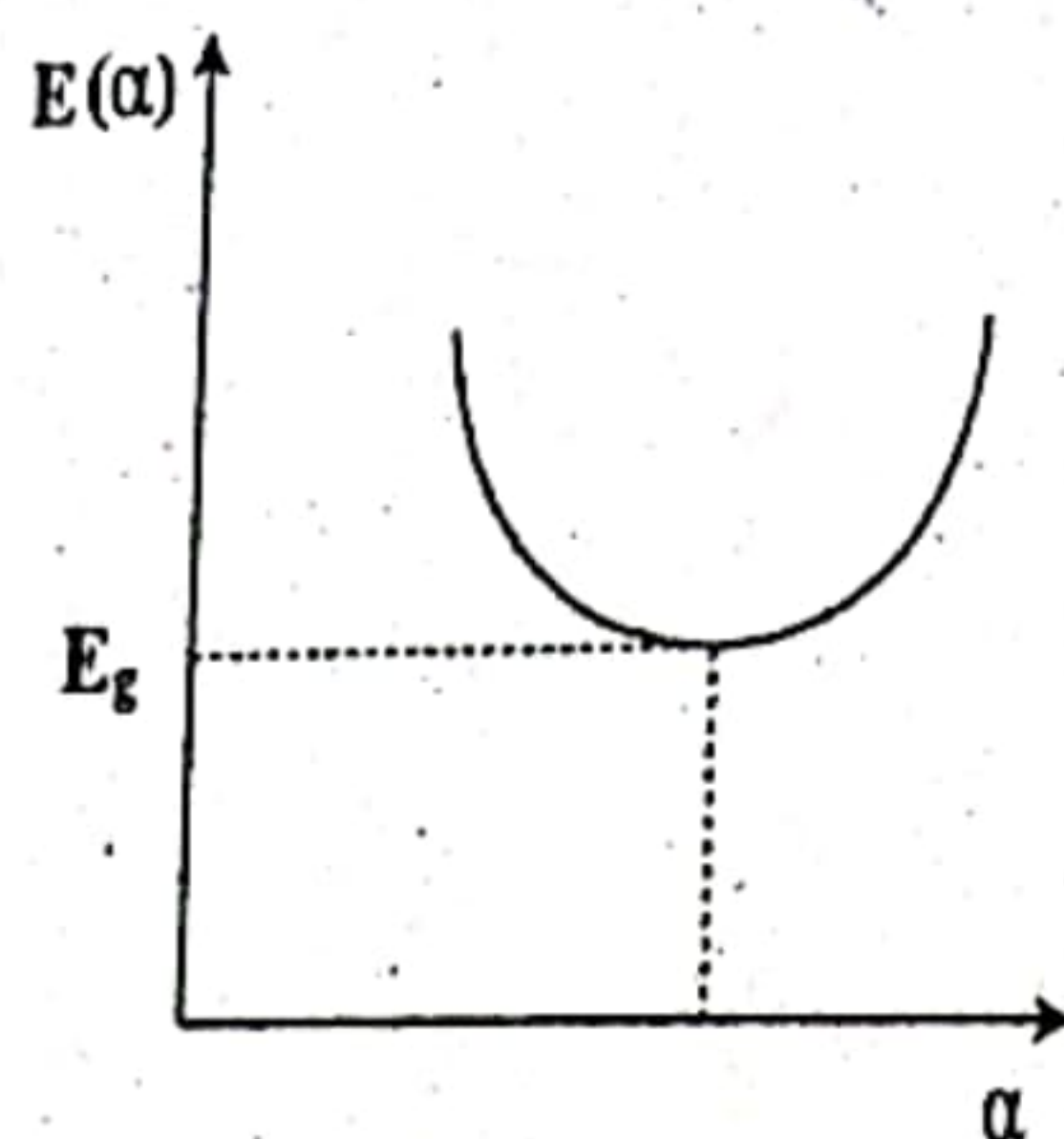
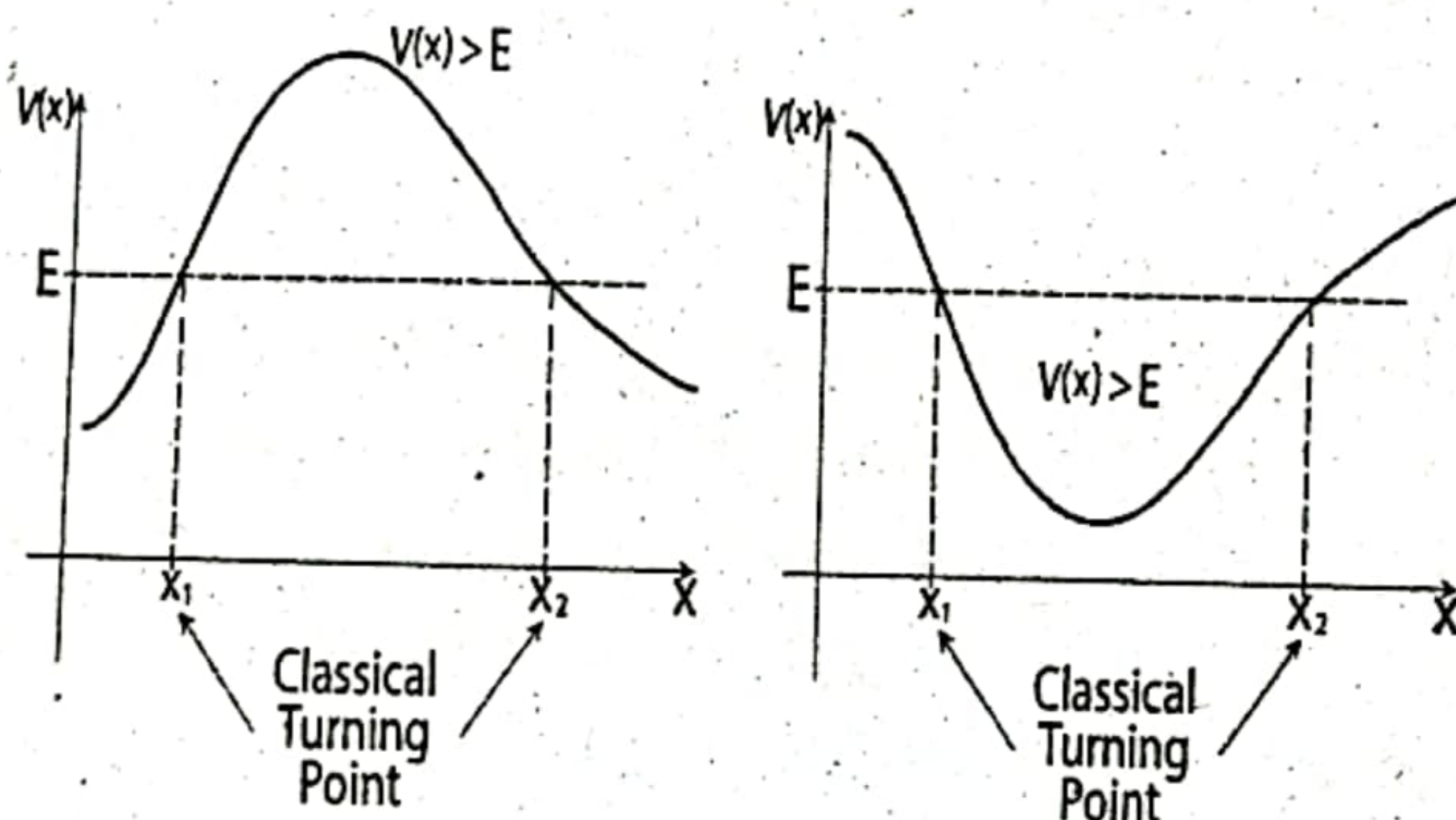


Fig. 2.3. Shape of ground state.

this property is always satisfied since the wavelength of classical system approaches zero. That's why it is called semi classical approximation. Consider the motion of a particle in


 Fig. 2.4. WKB approximation with energy E (a) $V(x) > E$ (b) $V(x) < E$.

a time independent potential $V(x)$, the Schrödinger equation of corresponding stationary state in one dimension is

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + V(x) \psi(x) = E \psi(x) \quad (2.27)$$

$$\frac{d^2}{dx^2} \psi(x) + k^2 \psi(x) = 0 \quad \text{for } E > V \text{ (Classical region)} \quad (2.28)$$

$$\therefore k = \frac{\sqrt{2m(E - V)}}{\hbar}$$

$$P = \hbar k = \sqrt{2m(E - V)} \quad (2.29)$$

$$\psi(x) = A e^{\pm i k x} \quad (2.30)$$

This is classical formula for $V(x)$ is constant: Classically the particle is confined within turning points. Now suppose $V(x)$ is not constant but varies slowly in comparison to λ . Then ψ is sinusoidal function and the wave length and the amplitude change slowly with x . So, Eq.(2.30) becomes

$$\psi(x) = A(x) e^{i\phi(x)} \quad (2.31)$$

Where the amplitude $A(x)$ and the phase $\phi(x)$ are real functions. Use prime to denote the derivative with respect to x .

$$\psi'(x) = \frac{d\psi}{dx} = (A' + iA\phi') e^{i\phi}$$

And,

$$\begin{aligned} \psi''(x) &= (A'' + i(A\phi'' + A'\phi')) e^{i\phi} + (A' + iA\phi') e^{i\phi} i\phi' \\ \psi''(x) &= \frac{d^2\psi}{dx^2} = [A'' + 2iA'\phi' + iA\phi'' - A(\phi')^2] e^{i\phi} \end{aligned}$$

Put in Eq.(2.28)

$$\begin{aligned} A'' + 2iA'\phi' + iA\phi'' - A(\phi')^2 &= -k^2 A \\ A'' + 2iA'\phi' + iA\phi'' - A(\phi')^2 &= -\frac{P^2}{\hbar^2} A \end{aligned}$$

This equation can be splitted into two equations, one for the real part and other for imaginary part. Imaginary part is

$$\begin{aligned} 2A'\phi' + A\phi'' &= 0 \\ (A^2\phi')' &= 0 \\ \therefore (A^2\phi')' &= A^2\phi'' + \phi' 2AA' = 0 \\ &= A\phi'' + 2A'\phi' = 0 \end{aligned}$$

By integration.

$$\begin{aligned} A^2\phi' &= C^2 \\ A &= \frac{C}{\sqrt{\phi'}} \end{aligned}$$

where C is an arbitrary real constant. Real part is

$$\begin{aligned} A'' - A(\phi')^2 &= -\frac{P^2}{\hbar^2} A \\ A'' &= A \left[(\phi')^2 - \frac{P^2}{\hbar^2} \right] \\ \frac{A''}{A} &= \left[(\phi')^2 - \frac{P^2}{\hbar^2} \right] \end{aligned} \quad (2.32)$$

For solving Eq(2.32), approximatively we assume that amplitude A varies slowly so that A'' term is very small and so $\frac{A''}{A}$ is negligible

$$\begin{aligned} (\phi')^2 - \frac{P^2}{\hbar^2} &= 0 \\ (\phi')^2 &= \frac{P^2}{\hbar^2} \\ \frac{d\phi}{dx} &= \pm \frac{P}{\hbar} \\ \phi(x) &= \pm \frac{1}{\hbar} \int P(x) dx \end{aligned}$$

So Eq(2.31) becomes

$$\psi_{\pm}(x) \cong \frac{C_{\pm}}{\sqrt{P(x)}} e^{\pm \frac{i}{\hbar} \int P(x) dx} \quad (2.33)$$

This is the solution of classically allowed region ($E > V$) where $P(x)$ is a real function. General (approximate) solution will be linear combination of two such terms, one with each sign i.e. $\psi_+(x)$ and $\psi_-(x)$.

$$\psi(x) = \frac{C_+}{\sqrt{P(x)}} e^{+\frac{i}{\hbar} \int P(x) dx} + \frac{C_-}{\sqrt{P(x)}} e^{-\frac{i}{\hbar} \int P(x) dx}$$

Above equation shows the wavefunction with oscillatory behaviour. The probability of finding the particle at x is inversely proportional to its (classical) momentum (velocity) at that point x $|\psi(x)|^2 \cong \frac{C}{P(x)}$. For classically forbidden region ($E < V$) Eq.(2.28) becomes

$$\frac{d^2}{dx^2} \psi(x) - k^2 \psi(x) = 0 \quad k^2 = \frac{2m(V - E)}{\hbar^2} \quad (2.34)$$

$$P = \hbar K = \sqrt{2m(V - E)} \quad (2.35)$$

As it is a bound particle

$$\psi(x) = Ae^{\pm Kx}$$

This is classical formula for $V(x)$ is constant. After similar calculations as we did in classically allowed region, the classical forbidden region wavefunction becomes

$$\psi_{\pm}(x) \cong \frac{C'_{\pm}}{\sqrt{|P(x)|}} e^{\pm \frac{1}{\hbar} \int |P(x)| dx}$$

In the form of linear combination

$$\psi(x) = \frac{C'_+}{\sqrt{P(x)}} e^{+\frac{1}{\hbar} \int P(x) dx} + \frac{C'_-}{\sqrt{|P(x)|}} e^{-\frac{1}{\hbar} \int P(x) dx}$$

Wavefunction is real showing exponentially decaying behaviour. Here, $P(x)$ is imaginary. For $E = V$, $k = 0$, $P(x) = 0$, $\psi(x) \rightarrow \infty$, $\lambda = \infty$. So, WKB method fails at the classical turning points. So, now we will deal with bound state problem to find the wavefunction. Before looking into that, let us first study the condition of validity for the WKB approximation.

$$\left| \frac{d\lambda}{dx} \right| \ll 1 \quad (2.36)$$

Bound States or Connection Formula

WKB method blows up at $x = 0$, $\Rightarrow P(x) = 0$, $\Rightarrow \psi(x) \rightarrow \infty$

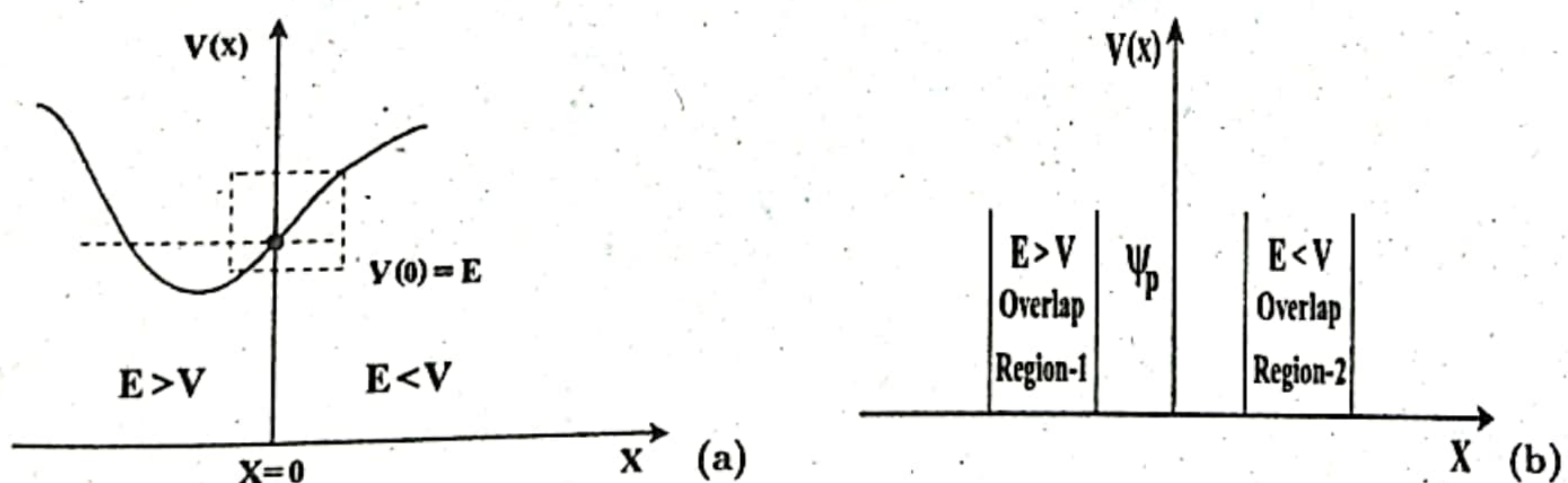


Fig. 2.5. (a) WKB fails at $x=0$ (b) Overlap region around ψ_p .

In WKB approximation, we have

$$\psi(x) \cong \begin{cases} \frac{1}{\sqrt{P(x)}} \left[B e^{\frac{i}{\hbar} \int_x^0 P(x') dx'} + C e^{-\frac{i}{\hbar} \int_x^0 P(x') dx'} \right] & x < 0 \\ \frac{1}{\sqrt{|P(x)|}} D e^{-\frac{1}{\hbar} \int_0^x |P(x')| dx'} & x > 0 \end{cases} \quad (2.37)$$

$V(x) < E$ for all $x < 0$ and $V(x) > E$ for all $x > 0$ and we can exclude the positive exponent in region $x > 0$ because, it blows up as $x \rightarrow \infty$. Our task is to join the two solutions at turning point ($x = 0$) as shown in Fig. (2.5). WKB fails at the vicinity of a turning point so we will use an approximation.

We will use a patching wave function ψ_p that will join the two WKB solutions. Patching wave function ψ_p in the neighborhood of turning point, uses a straight line ² potential whose slope is equal to the potential at the turning point.

$$V(x) \cong V(0) + \left. \frac{dV}{dx} \right|_{x=0} x$$

$$V(x) \cong E + V'(0)x$$

Solve the Schrödinger equation for this potential

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2 \psi_p}{dx^2} (E + V'(0)x) \psi_p &= E \psi_p \\ -\frac{\hbar^2}{2m} \frac{d^2 \psi_p}{dx^2} &= -V'(0)x \psi_p \\ \frac{d^2 \psi_p}{dx^2} &= \alpha^3 x \psi_p \quad \therefore \alpha^3 = \frac{2m}{\hbar^2} V'(0) \end{aligned} \quad (2.38)$$

Use substitutions $z = \alpha x$,

$$z^2 = \alpha^2 x^2$$

$$dz^2 = \alpha^2 dx^2$$

$$\alpha^2 \frac{d^2 \psi_p}{dz^2} = \alpha^3 x \psi_p \Rightarrow \frac{d^2 \psi_p}{dz^2} = \frac{z}{x} \psi_p$$

So, Eq.(2.38) becomes,

$$\frac{d^2 \psi_p}{dz^2} = z \psi_p$$

² Reference: $y = mx + c$

This is 2nd order differential equation of the form of airy's equation and hence the two solutions are called airy's functions, $A_i(z)$ and $B_i(z)$, where $z \gg 0$. Their linear combination gives patching wave function.

$$\psi_p(x) = a A_i(z) + b B_i(z)$$

$$A_i(z) \sim \frac{1}{2\sqrt{\pi}z^{1/4}} e^{-\frac{2}{3}z^{3/2}}$$

$$B_i(z) \sim \frac{1}{\sqrt{\pi}z^{1/4}} e^{+\frac{2}{3}z^{3/2}}$$

As shown in Fig. (2.5), now we have clear that ψ_p is overlapping in both the classically allowed and forbidden region. So, using Eq.(2.29) and Eq.(2.35)

Region-I ($x < 0$)

In region-I ($x < 0$), momentum is

$$\begin{aligned} P(x) &= \sqrt{2m(E - V(x))} \\ &= \sqrt{2m(-V(x))} \\ &= \sqrt{-\hbar^2 \alpha^3 x} \\ &= \hbar \alpha^{3/2} \sqrt{-x} \end{aligned}$$

Also,

$$\int_x^0 P(x') dx' = \frac{2}{3} \hbar (-\alpha x)^{3/2}$$

Region-II ($x > 0$)

In region-II ($x > 0$), momentum is

$$\begin{aligned} P(x) &= \sqrt{2m(E - V(x))} \\ &= \sqrt{2m(V(x))} \\ &= \sqrt{\hbar^2 \alpha^3 x} \\ &= \hbar \alpha^{3/2} \sqrt{x} \end{aligned}$$

Also,

$$\begin{aligned} \int_0^x |P(x')| dx' &= \hbar \alpha^{3/2} \int_0^x \sqrt{x'} dx' \\ &= \frac{2}{3} \hbar (\alpha x)^{3/2} \end{aligned}$$

WKB wave function Eq.(2.37) becomes

$$\begin{aligned} \psi(x) &= \frac{D}{\sqrt{\hbar \alpha^{3/4} x^{1/4}}} e^{-\frac{2}{3}(\alpha x)^{3/2}} & x > 0 \\ \psi(x) &= \frac{1}{\sqrt{\hbar \alpha^{3/4} (-x)^{1/4}}} \left[B e^{i\frac{2}{3}(-\alpha x)^{3/2}} + C e^{-i\frac{2}{3}(-\alpha x)^{3/2}} \right] & x < 0 \end{aligned}$$

Both these wave functions of region-I and region-II explains the particles including the turning point.

2.6 Review Questions

- 2.1 Differentiate between degenerate and non-degenerate states?
- 2.2 Why λ is regarded as strength of perturbation?
- 2.3 Show that $\sum_{\alpha=1}^f |a_{\alpha}|^2 = 1$, in time independent degenerate perturbation
- 2.4 Why we use the variational method for approximation?
- 2.5 Write down the equation of wave function for WKB approximation.
- 2.6 What is the validity of WKB approximation?
- 2.7 Write about the quantum tunneling in quantum mechanics.
- 2.8 Write down the condition for perturbation.
- 2.9 Show that the variational equation $\delta E(\psi) = 0$, is equivalent to Schrodinger equation.
- 2.10 Why we use the WKB approximation?



2.7 Solved Problems

- 2.1. A trial function ϕ differs from an eigen-function ψ_E so that $\phi = \psi_E + \alpha\phi_1$, where ψ_E and ϕ_1 are orthonormal and $\alpha \ll 1$. Show that $\langle H \rangle$ differs from E only by a term of order α^2 and find this term.

Solution

Given,

$$H\psi_E = E\psi_E$$

We have

$$\begin{aligned}\langle H \rangle &= \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\langle (\psi_E + \alpha\phi_1) | H | (\psi_E + \alpha\phi_1) \rangle}{\langle (\psi_E + \alpha\phi_1) | (\psi_E + \alpha\phi_1) \rangle} \\ \langle H \rangle &= \frac{\langle \psi_E | H | \psi_E \rangle + \alpha \langle \psi_E | H | \phi_1 \rangle + \alpha \langle \phi_1 | H | \psi_E \rangle + \alpha^2 \langle \phi_1 | H | \phi_1 \rangle}{\langle \psi_E | \psi_E \rangle + \alpha \langle \psi_E | \phi_1 \rangle + \alpha \langle \phi_1 | \psi_E \rangle + \alpha^2 \langle \phi_1 | \phi_1 \rangle}\end{aligned}$$

Since H is Hermitian,

$$\langle \psi_E | H | \phi_1 \rangle = E \langle \psi_E | \phi_1 \rangle = 0$$

$$\langle H \rangle = \frac{E + \alpha^2 \langle \phi_1 | H | \phi_1 \rangle}{1 + \alpha^2} = E + \alpha^2 \langle \phi_1 | H | \phi_1 \rangle$$

As $1 + \alpha^2 \cong 1$. Hence the result $\langle H \rangle$ differs from E by the term $\alpha^2 \langle \phi_1 | H | \phi_1 \rangle$.



2.2. The unperturbed wavefunction for Hamiltonian of harmonic oscillator is

$$\Psi_n^0(x) = \left(\frac{m\omega}{\hbar\pi} \right)^{1/4} \exp\left(-\frac{m\omega x^2}{2\hbar}\right)$$

If a small perturbation

$$V' = \begin{cases} \lambda x, & x > 0 \\ 0, & x \leq 0 \end{cases}$$

acts on the system, evaluate the first order correction to the ground state energy.

Solution

The given H_0 is the one dimensional simple harmonic oscillator. Hence the unperturbed ground state energy is

$$\psi_0^0(x) = \left(\frac{m\omega}{\hbar\pi} \right)^{1/4} \exp\left(-\frac{m\omega x^2}{2\hbar}\right)$$

The first order correction to the energy is

$$\begin{aligned} E_n^{(1)} &= \langle \psi_0(x) | \lambda x | \psi_0(x) \rangle \\ &= \left(\frac{m\omega}{\hbar\pi} \right)^{1/2} \lambda \int_0^\infty x \cdot \exp\left(-\frac{m\omega x^2}{\hbar}\right) dx \\ E_n^{(1)} &= \left(\frac{m\omega}{\hbar\pi} \right)^{1/2} \lambda \left(\frac{\hbar}{2m\omega} \right) \\ E_n^{(1)} &= \frac{\lambda}{2} \sqrt{\frac{\hbar}{\pi m\omega}} \end{aligned}$$



2.3. Solve the following one-dimensional infinite potential well, which is modified at the bottom by a perturbation $V_p(x)$

$$V(x) = \begin{cases} 0, & \text{for } 0 < x < a; \\ \infty, & \text{elsewhere;} \end{cases}$$

Calculate the energy E_n . Using the WKB method and compare it with the exact solution.

Solution

$V(x) = 0$ for $0 < x < a$ and $V(x) = \infty$ elsewhere. The turning points are $x_1 = 0$ and $x_2 = a$. The energy written the WKB approximation can be obtained using the quantization condition

$$\int_0^a P(E_n, x) dx = n\pi\hbar$$

$$\int_0^{a/2} \sqrt{2m(E - V_0)} dx + \int_{a/2}^a \sqrt{2mE} dx = n\pi\hbar$$

$$\frac{a}{2} \sqrt{2m} (\sqrt{E_n - V_0} + \sqrt{E_n}) = n\pi\hbar$$

$$2\sqrt{E_n(E_n - V_0)} \cdot \frac{a}{2} - 2E_n + V_0$$

$$4E_n^2 - 4E_n V_0 = a_n^2 + 4E_n^2 + V_0^2 - 4a_n E_n + 2a_n V_0 - 4E_n V_0$$

$$E_n = \frac{a_n^2}{4} + \frac{V_0}{2} + \frac{V_0^2}{4a_n}$$

As V_0 is small so neglect $V_0^2/4a_n$. The exact solution gives

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}, \quad n = 1, 2, 3, \dots,$$

The WKB solution has $(n + \frac{1}{2})$ in place of n . Another major difference is the allowed values of n .

$$E_n^{\text{WKB}} = \frac{\pi^2 \hbar^2}{2mL^2} n^2 + \frac{V_0}{2}$$



2.4. Use the WKB method to calculate the transmission coefficient of a particle of mass m and energy E moving in for the potential barrier

$$V(x) = \begin{cases} V_0 - ax, & x > 0 \\ 0, & x < 0 \end{cases}$$

Solution

The transmission coefficient is

$$T = \exp^{-2\gamma} \quad \therefore \quad \gamma = \frac{1}{\hbar} \int_{x_1}^{x_2} \sqrt{2m(V(x) - E)} dx$$

where that the turning point $x_1 = 0$. To get the other turning point, it is necessary that

$$E = V(x) = V_0 - ax_2$$

$$x_2 = \frac{V_0 - E}{a}$$

So, we get

$$\begin{aligned} \gamma &= \frac{1}{\hbar} \int_{x_1}^{x_2} \sqrt{2m(V(x) - E)} dx \\ &= \frac{\sqrt{2m}}{\hbar} \left| \frac{(V_0 - ax - E)^{3/2}}{-\frac{3}{2}a} \right|_0^{x_2} \\ &= \frac{-2\sqrt{2m}}{3a\hbar} \left[\left(V_0 - a \left(\frac{V_0 - E}{a} \right) - E \right)^{3/2} - (V_0 - E)^{3/2} \right] \\ &= \frac{-2\sqrt{2m}}{3a\hbar} \left[(0)^{3/2} - (V_0 - E)^{3/2} \right] \\ \gamma &= \frac{2\sqrt{2m}}{3a\hbar} (V_0 - E)^{3/2} \end{aligned}$$

Put in Above equation.

$$T = \exp \left[-\frac{4\sqrt{2m}}{3\hbar a} (V_0 - E)^{3/2} \right]$$

2.5. A particle of mass m moves in an infinite one-dimensional box of length $2a$ with a potential dip as defined by

$$V(x) = \begin{cases} \infty, & a < x < -a \\ -V_0, & -a < x < -\frac{a}{3} \\ 0, & -\frac{a}{3} < x < a \end{cases}$$

Find the energy of the ground state corrected to first order.

Solution

The unperturbed part of the Hamiltonian is that due to a particle in an infinite potential defined by $V(x)$ for $-a < x < a$ and $V(x) = \infty$ otherwise. The unperturbed ground state energy and eigen-functions are

$$E_1 = \frac{\pi^2 \hbar^2}{8ma^2}, \quad \psi_1 = \frac{1}{\sqrt{a}} \cos \frac{\pi x}{2a}$$

The perturbation $H' = -V_0$, $-a < x < -\frac{a}{3}$. The first order correction is

$$\begin{aligned} E^{(1)} &= -\frac{V_0}{a} \int_{-a}^{-\frac{a}{3}} \cos^2 \frac{\pi x}{2a} dx = -\frac{V_0}{2a} \int_{-a}^{-\frac{a}{3}} \left(1 + \cos \frac{\pi x}{a}\right) dx \\ &= -\frac{V_0}{a} \left|x\right|_{-a}^{-\frac{a}{3}} - \frac{V_0 a}{2a \pi} \left|\sin \frac{\pi x}{a}\right|_{-a}^{-\frac{a}{3}} \\ &= -\frac{V_0}{3} + \frac{V_0}{2\pi} \sin 60^\circ = -\frac{V_0}{3} + \frac{V_0}{2\pi} (0.866) \\ E_1^{(1)} &= 0.195V_0 \end{aligned}$$

The ground state energy corrected to first order is

$$E = \frac{\pi^2 \hbar^2}{8ma^2} = 0.195V_0$$

2.8 Multiple Choice Questions

- In non-degenerate time-independent perturbation theory the λ varies from
a) 0 to 1 b) 1 to 2 c) 0 to n d) None of these
- When the operator applying on a state and it gives the different eigen values
a) Symmetric b) degenerate c) Anti-symmetric d) Non-degenerate
- The operator changes in time while the Hamiltonian remains fixed in time
a) Dirac picture b) Heisenberg picture c) Schrödinger picture d) None of these
- WKB method can be viewed as approximation
a) Quantum mechanical b) Classical c) Semi-classical d) All of these
- Both basis and operators carry time dependence in
a) Heisenberg picture b) Dirac picture c) Schrodinger picture d) None of these
- Potential $V(r)$ slightly varies in
a) WKB b) Perturbation c) Variational d) All of these
- Variational principle states that
a) $E_g \leq E_n$ b) $E_g \geq E_n$ c) $E_g = E_n$ d) None of these
- WKB method is a technique for obtaining solutions in
a) One dimension b) Two dimension c) Three dimension d) All of these
- Variational method is used to find the approximation to the state
a) Excited state b) Ground state c) Intermediate state d) None of these
- The wave function becomes in WKB approximation when $E = V(r)$
a) Real b) Imaginary c) Infinite d) None of these

Answers

1	a	2	b	3	c	4	c	5	b
6	a	7	a	8	d	9	b	10	c

Chapter 3

Time Dependent Perturbation Theory

3.1 Time Evolution of a System

The time evolution of the state vector $|\psi(0)\rangle$ or $|\psi(t_i)\rangle$ of a system is managed by the time-dependent Schrödinger equation.

$$\boxed{i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} = \hat{H} |\psi(t)\rangle,} \quad (3.1)$$

where $\hat{H}$ is the time independent Hamiltonian operator corresponding to the total energy of the system. We want to examine here how quantum states evolve with time. That is, consider the initial state $|\psi(t_i)\rangle$, where t_i is the instant of initial observation. How does one find the state $|\psi(t)\rangle$ at any later time t . The two states can be related by means of a linear operator $\hat{U}(t, t_i)$, such that

$$|\psi(t)\rangle = \hat{U}(t, t_i) |\psi(t_i)\rangle$$

where $\hat{U}(t, t_i)$ is known as the time evolution operator or propagator and is defined as

$$\boxed{\hat{U}(t, t_i) = e^{-i(t-t_i)\hat{H}/\hbar}}$$

$\hat{U}^\dagger(t, t_i)$ is unitary transformation operator for which $\hat{U}(t, t_i) \hat{U}^\dagger(t, t_i) = \hat{I}$. Thus, one can also write as $|\psi(t_i)\rangle = \hat{U}^\dagger(t, t_i) |\psi(t)\rangle$

3.2 Time Dependent Perturbation Theory

This is one of the most important approximation theory because almost all the systems are time dependent. One of the best example is the process of absorption and emission of radiation by atoms or molecules. In this theory, we consider those phenomena that are described by Hamiltonian which can be split into two parts.

- (i) time independent part $\hat{H}_0$ or free Hamiltonian part $\hat{H}_0$.
- (ii) time dependent part $\hat{V}(t)$ or interacting Hamiltonian part $\hat{V}(t)$. This is small compared to $\hat{H}_0$.

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$$

Consider a system which when unperturbed, is described by a time independent Hamiltonian ($\hat{H}_0$) whose exact solution, the eigen value E_n and eigen state, $|\psi_n\rangle$ are known

$$\hat{H}_0 |\psi_n\rangle = E_n |\psi_n\rangle$$

Moreover, the most general state vectors are given by stationary states.

$$|\Psi_n(t)\rangle = \underbrace{e^{\frac{-itE_n}{\hbar}}}_{\text{phase factor}} |\psi_n\rangle$$

In the time interval, we subject the system to an external time dependent perturbation $\hat{V}(t)$, that is small compared to $\hat{H}_0$.

$$\hat{V}(t) = \begin{cases} \hat{V}(t) & ; \quad 0 \leq t \leq \tau \\ 0 & ; \quad t < 0, t > \tau \end{cases}$$

Here, τ is the time for which the system was perturbed. However, before and after this time τ , the system was unperturbed. Thus, $\hat{V}(t)$ exists only in the duration of transition. The full Hamiltonian of the system is $\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$ and the corresponding Schrödinger equation is

$$\begin{aligned} E |\Psi(t)\rangle &= \hat{H}(t) |\Psi(t)\rangle \\ i\hbar \frac{d}{dt} |\Psi(t)\rangle &= (\hat{H}_0 + \hat{V}(t)) |\Psi(t)\rangle \end{aligned} \quad (3.2)$$

Where $\hat{V}(t)$ gives the interaction of the system with the external source of perturbation. When the system interact with $\hat{V}(t)$, it either absorbs or emits energy. This process causes the system to undergo transition from one unperturbed eigen state $|\Psi_{(t_i)}\rangle$ to another eigen state $|\Psi_{(t_f)}\rangle$. Here, we will work in the interaction picture.

We are dealing with time dependent potentials and it is more convenient to solve Schrödinger equation in the interaction picture. So, Eq.(3.2) becomes in interaction picture

$$i\hbar \frac{d}{dt} |\Psi_{(t)}\rangle_I = \hat{V}_I(t) |\Psi_{(t)}\rangle_I, \quad (3.3)$$

where

$$|\Psi_{(t)}\rangle_I = e^{i\hat{H}_0 t/\hbar} |\Psi_{(t)}\rangle \quad (3.4)$$

$$\hat{V}_I(t) = e^{i\hat{H}_0 t/\hbar} \hat{V}(t) e^{-i\hat{H}_0 t/\hbar} \quad (3.5)$$

Calculation of $|\Psi_{(t)}\rangle_I$

The time evolution equation is given by unitary operator

$$|\Psi_{(t)}\rangle = \hat{U}(t, t_i) |\Psi_{(t_i)}\rangle \quad (3.6)$$

Putting the value of $|\Psi_{(t)}\rangle$ from Eq.(3.6) in Eq.(3.4)

$$|\Psi_{(t)}\rangle_I = e^{\frac{i\hat{H}_0 t}{\hbar}} \hat{U}(t, t_i) |\Psi_{(t_i)}\rangle \quad (3.7)$$

Calculation of $\hat{U}_I(t, t_i)$

From Eq.(3.4)

$$\begin{aligned} \frac{1}{e^{\frac{i\hat{H}_0 t}{\hbar}}} |\Psi_{(t)}\rangle_I &= |\Psi_{(t)}\rangle \\ e^{\frac{-i\hat{H}_0 t}{\hbar}} |\Psi_{(t)}\rangle_I &= |\Psi_{(t)}\rangle \end{aligned}$$

Let $t = t_i$, above equation becomes

$$|\Psi_{(t_i)}\rangle = e^{\frac{-i\hat{H}_0 t_i}{\hbar}} |\Psi_{(t_i)}\rangle_I$$

Putting this value in Eq.(3.7)

$$|\Psi(t)\rangle_I = e^{\frac{iH_0 t}{\hbar}} \hat{U}(t, t_i) e^{-\frac{iH_0 t_i}{\hbar}} |\Psi(t_i)\rangle_I$$

$$|\Psi(t)\rangle_I = \hat{U}_I(t, t_i) |\Psi(t_i)\rangle_I$$

$$\therefore \hat{U}_I(t, t_i) = e^{\frac{iH_0 t}{\hbar}} \hat{U}(t, t_i) e^{-\frac{iH_0 t_i}{\hbar}}$$

Putting these values in Eq.(3.3), we get

$$i\hbar \frac{d}{dt} \hat{U}_I(t, t_i) |\Psi(t_i)\rangle_I = \hat{V}_I(t) \hat{U}_I(t, t_i) |\Psi(t_i)\rangle_I$$

Canceling $|\Psi(t_i)\rangle_I$ ($\therefore$ constant) on both sides we get,

$$i\hbar \frac{d}{dt} \hat{U}_I(t, t_i) = \hat{V}_I(t) \hat{U}_I(t, t_i)$$

$$i\hbar d \hat{U}_I(t, t_i) = \hat{V}_I(t) \hat{U}_I(t, t_i) dt$$

Integrate both sides using boundary condition $\hat{U}_I(t_i, t_i) = I$ and taking t' as the changing time from t_i to t .

$$\int_{t_i}^t i\hbar d \hat{U}_I(t', t_i) = \int_{t_i}^t \hat{V}_I(t') \hat{U}_I(t', t_i) dt'$$

Multiply both sides with i , then multiply with $-$ and divide by $\hbar$

$$\int_{t_i}^t d \hat{U}_I(t', t_i) = -\frac{i}{\hbar} \int_{t_i}^t \hat{V}_I(t') \hat{U}_I(t', t_i) dt'$$

$$\hat{U}_I(t, t_i) - 1 = -\frac{i}{\hbar} \int_{t_i}^t \hat{V}_I(t') \hat{U}_I(t', t_i) dt'$$

$$\hat{U}_I(t, t_i) = 1 - \frac{i}{\hbar} \int_{t_i}^t \hat{V}_I(t') \hat{U}_I(t', t_i) dt' \quad (3.8)$$

Time dependent perturbation theory provides approximate solution to this integral equation, we assume that $\hat{V}_I(t')$ is small. The first order approximation is obtained by putting $\hat{U}_I(t', t_i) = 1$ and $\hat{U}_I(t, t_i) = \hat{U}_I^{(1)}(t, t_i)$ in Eq.(3.8)

$$\hat{U}_I^{(1)}(t, t_i) = 1 - \frac{i}{\hbar} \int_{t_i}^t \hat{V}_I(t') dt'$$

The second order approximation is obtained by putting $\hat{U}_I(t, t_i) = \hat{U}_I^{(2)}(t, t_i)$ and $\hat{U}_I(t', t_i) = \hat{U}_I^{(1)}(t', t_i)$ in Eq.(3.8)

$$\hat{U}_I^{(2)}(t, t_i) = 1 - \frac{i}{\hbar} \int_{t_i}^t \hat{V}_I(t') dt' + \left(\frac{-i}{\hbar}\right)^2 \int_{t_i}^t \hat{V}_I(t_1) dt_1 \int_{t_i}^{t_1} \hat{V}_I(t_2) dt_2$$

The third order approximation is obtained by saying $\hat{U}_I^{(3)}(t, t_i)$ in Eq.(3.8) and so on. The repetition of this interaction process gives.

$$\begin{aligned} \hat{U}_I^{(n)}(t, t_i) = & 1 - \frac{i}{\hbar} \int_{t_i}^t \hat{V}_I(t') dt' + \left(\frac{-i}{\hbar}\right)^2 \int_{t_i}^t \hat{V}_i(t_1) dt_1 \int_{t_i}^{t_1} \hat{V}_i(t_2) dt_2 + \dots \\ & + \left(\frac{-i}{\hbar}\right)^n \int_{t_i}^t \hat{V}_i(t_1) dt_1 \int_{t_i}^{t_1} \hat{V}_i(t_2) dt_2 \int_{t_i}^{t_2} \hat{V}_i(t_3) dt_3 \dots \int_{t_i}^{t_{n-1}} \hat{V}_i(t_n) dt_n + \dots \end{aligned} \quad (3.9)$$

This series known as the Dyson series, allows for the calculation of the state vector up to desired order in the perturbation. By using this, we can calculate the transition probability. It can be obtained by taking the matrix elements of Eq.(3.9) between the eigen states of $\hat{H}_0$. Here, we have $t_1 > t_2 > \dots > t_n$, so we can say that its a time ordered equation.

3.3 Transition Probability

The transition probability corresponding to a transition from an initial unperturbed state $|\psi_i\rangle$ to another state $|\psi_f\rangle$ is obtained from Eq.(3.9)

$$P_{if}(t) = \left| \langle \psi_f | \hat{U}_I(t, t_i) | \psi_i \rangle \right|^2$$

Put Dyson series up to 1st order because higher order are hard to control

$$\begin{aligned} P_{if}(t) = & \left| \langle \psi_f | 1 - \frac{i}{\hbar} \int_0^t \hat{V}_I(t') dt' + \dots | \psi_i \rangle \right|^2 \\ P_{if}(t) = & \left| \langle \psi_f | \psi_i \rangle - \langle \psi_f | \frac{i}{\hbar} \int_0^t \hat{V}_I(t') dt' | \psi_i \rangle + \dots \right|^2 \end{aligned}$$

$$P_{if}(t) = \left| \langle \psi_f | \psi_i \rangle - \langle \psi_f | \frac{i}{\hbar} \int_0^t \hat{V}(t') e^{i\omega_{fi}t'} dt' | \psi_i \rangle + \dots \right|^2 \quad (3.10)$$

Where we have used the fact that

$$\langle \psi_f | \hat{V}_I(t') | \psi_i \rangle = \langle \psi_f | e^{i\hat{H}_0 t'/\hbar} \hat{V}(t') e^{-i\hat{H}_0 t'/\hbar} | \psi_i \rangle = \langle \psi_f | V(t') e^{i\omega_{fi}t'} | \psi_i \rangle = \langle \psi_f | \hat{V}(t') | \psi_i \rangle e^{i\omega_{fi}t'}$$

Where the transition frequency¹ between the initial (i) and final (f) state is,

$$\omega_{fi} = \frac{E_f - E_i}{\hbar}$$

$$\omega_{fi} = \frac{1}{\hbar} (\langle \psi_f | \hat{H}_0 | \psi_f \rangle - \langle \psi_i | \hat{H}_0 | \psi_i \rangle)$$

The first order transition probability for $|\psi_i\rangle \rightarrow |\psi_f\rangle$ (and hence $\langle \psi_f | \psi_i \rangle = 0$) is obtained by terminating Eq.(3.10) at the first order in $\hat{V}_I(t)$

$$P_{if}(t) = \left| -\frac{i}{\hbar} \int_0^t \langle \psi_f | \hat{V}(t') | \psi_i \rangle e^{i\omega_{fi}t'} dt' \right|^2 \quad (3.11)$$

We can use Eq.(3.10) to calculate the transition probability to any order in $\hat{V}_I(t)$. However, the terms higher than the first order become rapidly intractable. For most problems of atomic and nuclear physics, the first order Eq.(3.11) is usually sufficient. We apply Eq.(3.11) to calculate transition probability for two cases.

- (i) A Constant Perturbation (time independent)
- (ii) A Harmonic Perturbation (time dependent)

Transition Probability for a Constant Perturbation

In this case, where $\hat{V}$ does not depend on time i.e. $\hat{V}(t) = \hat{V}$, Eq.(3.11) leads to

$$P_{if}(t) = \left| -\frac{i}{\hbar} \int_0^t \langle \psi_f | \hat{V} | \psi_i \rangle e^{i\omega_{fi}t'} dt' \right|^2$$

¹ $\Delta E = \hbar\omega \Rightarrow \omega = \Delta E/\hbar \Rightarrow \omega_{fi} = \frac{E_f - E_i}{\hbar}$

$$P_{if}(t) = \frac{1}{\hbar^2} \left| \langle \psi_f | \hat{V} | \psi_i \rangle \int_0^t e^{i\omega_{fi}t'} dt' \right|^2$$

$$P_{if}(t) = \frac{1}{\hbar^2} \left| \langle \psi_f | \hat{V} | \psi_i \rangle \right|^2 \left| \frac{e^{i\omega_{fi}t} - 1}{i\omega_{fi}} \right|^2$$

$$P_{if}(t) = \frac{1}{\hbar^2} \left| \langle \psi_f | \hat{V} | \psi_i \rangle \right|^2 \left| \frac{e^{i\omega_{fi}t} - 1}{\omega_{fi}} \right|^2$$

$$P_{if}(t) = \frac{1}{\hbar^2 \omega_{fi}^2} \left| \langle \psi_f | \hat{V} | \psi_i \rangle \right|^2 \left| e^{i\omega_{fi}t} - 1 \right|^2$$

As $|e^{i\theta} - 1|^2 = 4\sin^2(\frac{\theta}{2})$, so $|e^{i\omega_{fi}t} - 1|^2 = 4\sin^2(\frac{\omega_{fi}t}{2})$

$$P_{if}(t) = \frac{4 \left| \langle \psi_f | \hat{V} | \psi_i \rangle \right|^2}{\hbar^2 \omega_{fi}^2} \sin^2\left(\frac{\omega_{fi}t}{2}\right)$$

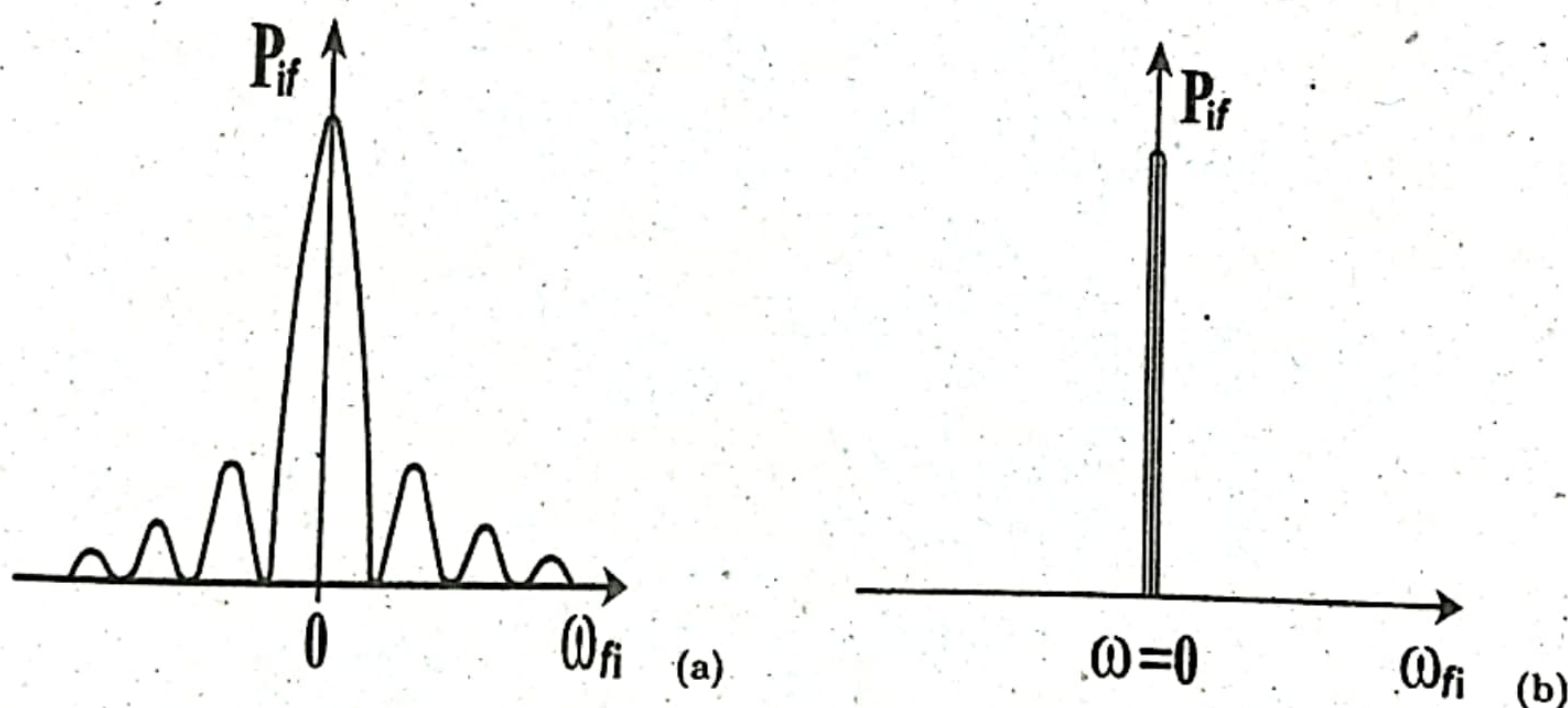


Fig. 3.1. (a) Plot of perturbation for a fixed value of t (b) Plot of perturbation as delta function at $t \rightarrow \infty$.

As a function of ω_{fi} , the transition probability has an interference pattern as shown in Fig.(3.1(a)) it is appreciable only near $\omega_{fi} = 0$ and decays rapidly as ω_{fi} moves away from zero. This means the transition probability of finding the system in a state $|\psi_f\rangle$ of energy E_f is greatest only when E_i and E_f are close enough that energy gap is very small (see Fig. (3.2)). $E_i = E_f$ or when $\omega_{fi} = 0$. The height and width of central peak are proportional to $t^2 = 1/\omega_{fi}^2$ and $\frac{1}{t} = \omega_{fi}$ respectively, so the area under the curve is proportional to t . We see that most of the area is under the central peak around $\omega_{fi} = 0$, the transition

probability is proportional to t . The central peak becomes narrower and higher as time increases, this is exactly the property of delta function ². Thus, in the limit $t \rightarrow \infty$, the transition probability takes the shape of delta function (as shown in Fig.(3.1(b))).

$$\lim_{t \rightarrow \infty} \frac{\sin^2(yt)}{\pi y^2 t} = \delta(y)$$

We can write ($\because y = \frac{\omega_{fi} t}{2}$),

$$\lim_{t \rightarrow \infty} \frac{\sin^2(\frac{\omega_{fi} t}{2})}{\pi (\frac{1}{2} \omega_{fi})^2 t} = \delta\left(\frac{\omega_{fi}}{2}\right)$$

$$\therefore \delta\left(\frac{\omega_{fi}}{2}\right) = 2\hbar \delta(\hbar \omega_{fi})$$

So above equation becomes,

$$\sin^2\left(\frac{\omega_{fi} t}{2}\right) = \pi t \times \frac{1}{4} \omega_{fi}^2 \times 2\hbar \delta(\hbar \omega_{fi})$$

$$\sin^2\left(\frac{\omega_{fi} t}{2}\right) = 2\pi \hbar t \times \frac{1}{4} \omega_{fi}^2 \delta(\hbar \omega_{fi}) \quad (3.12)$$

Also, $\hbar \omega_{fi} = E_f - E_i$

$$\delta(\hbar \omega_{fi}) = \delta(E_f - E_i)$$

So Eq.(3.12) becomes,

$$\sin^2\left(\frac{\omega_{fi} t}{2}\right) = 2\pi \hbar t \times \frac{1}{4} \omega_{fi}^2 \delta(E_f - E_i)$$

Putting this value in Eq.(3.3)

$$P_{if}(t) = \frac{4 |\langle \psi_f | \hat{V} | \psi_i \rangle|^2}{\hbar^2 \omega_{fi}^2} \times 2\pi \hbar t \times \frac{1}{4} \omega_{fi}^2 \delta(E_f - E_i)$$

$$P_{if}(t) = \frac{2\pi t}{\hbar} |\langle \psi_f | \hat{V} | \psi_i \rangle|^2 \delta(E_f - E_i)$$

The transition rate which is defined as a transition probability per unit time and is given by,

$$\Gamma_{if}(t) = \frac{P_{if}(t)}{t}$$

Putting the value from above equation,

² Delta function means there is only maximum value at any given point. (see Fig. (3.1)(b))

$$\Gamma_{if}(t) = \frac{\frac{2\pi t}{\hbar} |\langle \psi_f | \hat{V} | \psi_i \rangle|^2 \delta(E_f - E_i)}{t}$$

$$\Gamma_{if}(t) = \frac{2\pi}{\hbar} |\langle \psi_f | \hat{V} | \psi_i \rangle|^2 \delta(E_f - E_i) \quad (3.13)$$

The delta term $\delta(E_f - E_i)$ generates the conservation of energy in the limit $t \rightarrow \infty$, the transition rate is non-vanishing only between states of equal energy. Hence, a constant (time independent) perturbation neither removes energy from the system nor supplies energy to it. It simply causes energy-conserving transitions (see Fig. (3.2)).

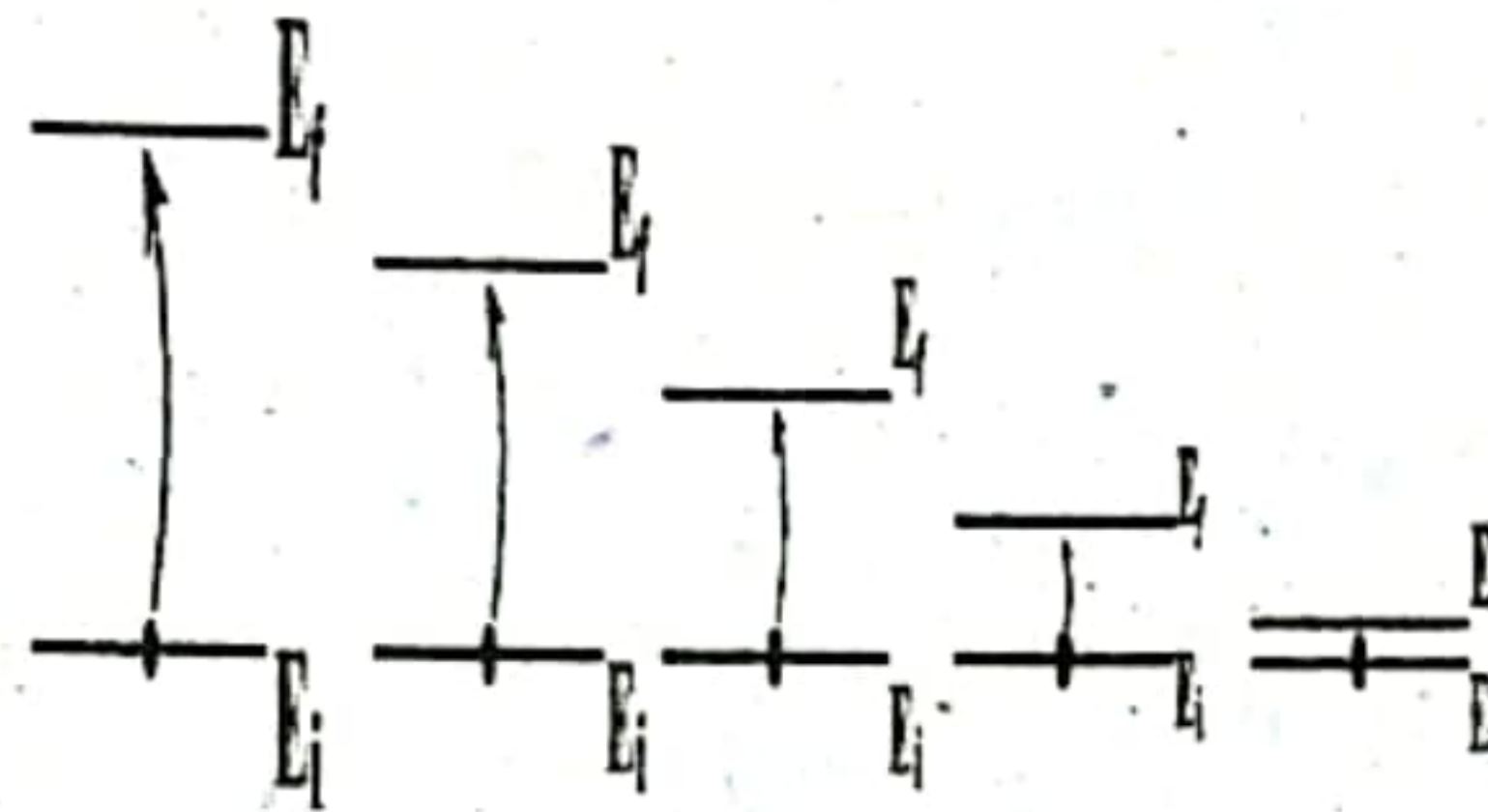


Fig. 3.2. A schematic picture of transition from E_i to E_f and finally reaching to $E_i = E_f$.

Transition into a Continuum of Final States

We calculate total transition rate from an initial state $|\psi_i\rangle$ into a continuum of final state $|\psi_f\rangle$.

The number of final states per unit energy interval $= \rho(E_f)$

The number of final states with energy interval E_f and $E_f + dE_f = \rho(E_f)dE_f$

The total transition rate W_{if} can be obtained by multiplying Eq.(3.13) by $\rho(E_f)dE_f$ and then integrating.

$$W_{if} = \frac{2\pi}{\hbar} |\langle \psi_f | \hat{V} | \psi_i \rangle|^2 \rho(E_f) \delta(E_f - E_i) dE_f$$

But $\rho(E_f) \delta(E_f - E_i) dE_f = \rho(E_i)$, So above equation becomes

$$W_{if} = \frac{2\pi}{\hbar} |\langle \psi_f | \hat{V} | \psi_i \rangle|^2 \rho(E_i) \quad (3.14)$$

This relation is called the **Fermi golden rule**. This shows that in case of constant perturbation, if we wait long enough, the total transition rate becomes constant (time independent).

Transition Probability for a Harmonic Perturbation

Consider a perturbation which depends harmonically on time (the time between the moments of turning the perturbation ON and OFF). Harmonic perturbation is given as

$$\hat{V}(t') = \underbrace{\hat{v} e^{-i\omega t'}}_{\text{Absorption}} + \underbrace{\hat{v}^\dagger e^{+i\omega t'}}_{\text{Emission}}, \quad (3.15)$$

Where $\hat{v}$ and $\hat{v}^\dagger$ are time independent operators. The transition probability corresponding to this perturbation can be obtained by putting Eq.(3.15) in Eq.(3.11).

$$\begin{aligned} P_{if}(t) &= \left| -\frac{i}{\hbar} \int_0^t \langle \psi_f | \hat{V}(t') | \psi_i \rangle e^{i\omega_f t'} dt' \right|^2 \\ P_{if}(t) &= \left| -\frac{i}{\hbar} \int_0^t \langle \psi_f | (\hat{v} e^{-i\omega t'} + \hat{v}^\dagger e^{+i\omega t'}) | \psi_i \rangle e^{i\omega_f t'} dt' \right|^2 \\ P_{if}(t) &= \frac{1}{\hbar^2} \left| \int_0^t \langle \psi_f | \hat{v} e^{i(\omega_f - \omega)t'} dt' | \psi_i \rangle + \int_0^t \langle \psi_f | \hat{v}^\dagger e^{i(\omega_f + \omega)t'} dt' | \psi_i \rangle \right|^2 \\ P_{if}(t) &= \frac{1}{\hbar^2} \left| \langle \psi_f | \hat{v} | \psi_i \rangle \int_0^t e^{i(\omega_f - \omega)t'} dt' \right|^2 + \frac{1}{\hbar^2} \left| \langle \psi_f | \hat{v}^\dagger | \psi_i \rangle \int_0^t e^{i(\omega_f + \omega)t'} dt' \right|^2 \end{aligned}$$

Solving,

$$\begin{aligned} \left| \int_0^t e^{i(\omega_f - \omega)t'} dt' \right|^2 &= \left| \left[\frac{e^{i(\omega_f - \omega)t'}}{i(\omega_f - \omega)} \right]_0^t \right|^2 \\ &= \left| \frac{e^{i(\omega_f - \omega)t} - e^0}{i(\omega_f - \omega)} \right|^2 \\ \left| \int_0^t e^{i(\omega_f - \omega)t'} dt' \right|^2 &= \left| \frac{e^{i(\omega_f - \omega)t} - 1}{i(\omega_f - \omega)} \right|^2 \end{aligned}$$

Similarly,

$$\left| \int_0^t e^{i(w_{fi}+w)t'} dt' \right|^2 = \frac{|e^{i(w_{fi}+w)t} - 1|^2}{(w_{fi} + w)^2}$$

So Eq.(3.3) become,

$$P_{if}(t) = \frac{1}{\hbar^2} |\langle \psi_f | \hat{v} | \psi_i \rangle|^2 \frac{|e^{i(w_{fi}-w)t} - 1|^2}{(w_{fi} - w)^2} + \frac{1}{\hbar^2} |\langle \psi_f | \hat{v}^\dagger | \psi_i \rangle|^2 \frac{|e^{i(w_{fi}+w)t} - 1|^2}{(w_{fi} + w)^2} \quad (3.16)$$

Using,

$$\begin{aligned} |e^{i\theta} - 1|^2 &= 4 \sin^2 \frac{\theta}{2} \\ \Rightarrow |e^{i(w_{fi}-w)t} - 1|^2 &= 4 \sin^2 \frac{(w_{fi} - w)t}{2} \\ \Rightarrow |e^{i(w_{fi}+w)t} - 1|^2 &= 4 \sin^2 \frac{(w_{fi} + w)t}{2} \end{aligned}$$

$$P_{if}(t) = \frac{4}{\hbar^2} |\langle \psi_f | \hat{v} | \psi_i \rangle|^2 \frac{\sin^2(w_{fi} - w)t/2}{(w_{fi} - w)^2} + \frac{4}{\hbar^2} |\langle \psi_f | \hat{v}^\dagger | \psi_i \rangle|^2 \frac{\sin^2(w_{fi} + w)t/2}{(w_{fi} + w)^2}$$

Fig.(3.3) plot of P_{if} versus w_{fi} , for a fixed value of t . In the Fig.(3.3) the transition probability at $w_{fi} = \pm w$, where its maximum value is

$$P_{if}(t) = \left(\frac{t^2}{4\hbar^2} \right) |\langle \psi_f | \hat{v} | \psi_i \rangle|^2 \quad (\text{Absorption})$$

At $w_{fi} = -w$, where its maximum value is.

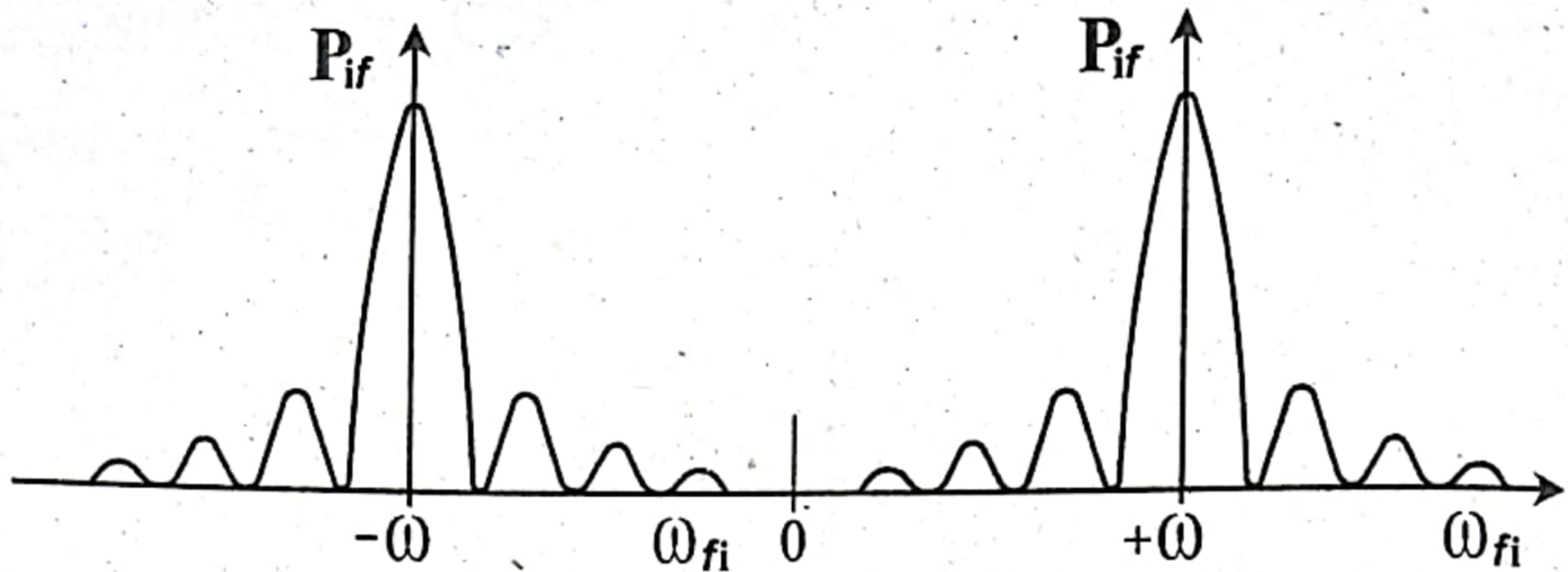
$$P_{if}(t) = \left(\frac{t^2}{4\hbar^2} \right) |\langle \psi_f | \hat{v}^\dagger | \psi_i \rangle|^2 \quad (\text{Emission})$$

The probability of transition is greatest only when the frequency of the perturbing field is close to $\pm w_{fi}$. As w moves away from $\pm w_{fi}$, P_{if} decreases rapidly. To study emission and absorption clearly, we use the limit $t \rightarrow \infty$.

$$\lim_{t \rightarrow \infty} \frac{\sin^2(yt)}{\pi y^2 t} = \delta(y)$$

Here $y (= \frac{w_{fi} \pm w}{2})$ so,

$$\frac{\sin^2(\frac{w_{fi} \pm w}{2} t)}{\frac{1}{4} \pi (w_{fi} \pm w)^2 t} = \delta\left(\frac{w_{fi} \pm w}{2}\right) \quad (3.17)$$

Fig. 3.3. Plots of harmonic perturbation for a fixed value of t .

Also,

$$\delta\left(\frac{w_{fi} + w}{2}\right) = 2\hbar\delta\{\hbar(w_{fi} + w)\}$$

$$\delta\left(\frac{w_{fi} + w}{2}\right) = 2h\delta(\hbar w_{fi} + \hbar w)$$

Also, $\hbar w_{fi} = E_f - E_i$. Putting the value in above equation

$$\delta\left(\frac{w_{fi} + w}{2}\right) = 2h\delta(E_f - E_i + \hbar w)$$

So Eq.(3.17) becomes,

$$\frac{\sin^2\left(\frac{w_{fi} + w}{2}t\right)}{\frac{1}{4}\pi(w_{fi} + w)^2 t} = 2h\delta(E_f - E_i + \hbar w)$$

$$\frac{\sin^2\left(\frac{w_{fi} + w}{2}t\right)}{(w_{fi} + w)^2} = \frac{1}{4}\pi t \times 2h\delta(E_f - E_i + \hbar w)$$

$$\frac{\sin^2\left(\frac{w_{fi} + w}{2}t\right)}{(w_{fi} + w)^2} = \frac{1}{2}\pi t \times h\delta(E_f - E_i + \hbar w) \quad (3.18)$$

Similarly,

$$\frac{\sin^2\left(\frac{w_{fi} - w}{2}t\right)}{(w_{fi} - w)^2} = \frac{1}{2}\pi t \times h\delta(E_f - E_i - \hbar w) \quad (3.19)$$

Putting values from Eq.(3.18) and Eq.(3.19) in Eq.(3.16) and dividing by t , we can obtain transition rate.

$$\frac{P_{if}}{t} = \frac{4}{\hbar^2 t} |\langle \psi_f | \hat{v} | \psi_i \rangle|^2 \times \frac{1}{2} \pi \hbar \delta(E_f - E_i - \hbar \omega) + \frac{4}{\hbar^2 t} |\langle \psi_f | \hat{v}^\dagger | \psi_i \rangle|^2 \times \frac{1}{2} \pi \hbar \delta(E_f - E_i + \hbar \omega)$$

$$\Gamma_{if} = \frac{2\pi}{\hbar} |\langle \psi_f | \hat{v} | \psi_i \rangle|^2 \delta(E_f - E_i - \hbar \omega) + \frac{2\pi}{\hbar} |\langle \psi_f | \hat{v}^\dagger | \psi_i \rangle|^2 \delta(E_f - E_i + \hbar \omega) \quad (3.20)$$

The transition rate ($\frac{P_{if}}{t} = \Gamma_{if}$) is non-zero only when either of the following two conditions are satisfied.

$$\begin{aligned} E_f - E_i = -\hbar \omega &\Rightarrow E_f = E_i - \hbar \omega \quad (\text{i.e. } E_f < E_i \quad \text{Emission}) \\ E_f - E_i = \hbar \omega &\Rightarrow E_f = E_i + \hbar \omega \quad (\text{i.e. } E_f > E_i \quad \text{Absorption}) \end{aligned}$$

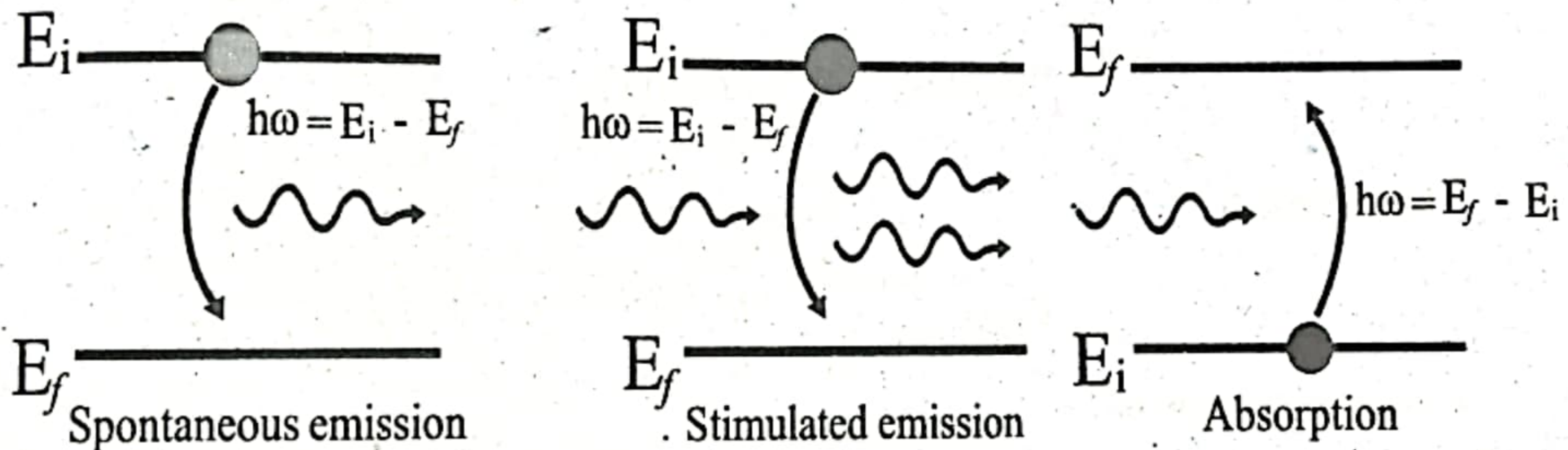


Fig. 3.4. Spontaneous, stimulated emission and absorption of a photon of energy $\hbar \omega$

These two situations cannot be satisfied simultaneously. The first condition $E_f = E_i - \hbar \omega$ (Emission) implies that the system is initial in excited state because its final energy is smaller than the initial energy; when acted upon by the perturbation, the system de-excites by giving up a photon of energy $\hbar \omega$ as shown in Fig.(3.4). The process is called stimulated emission because the system emits a photon of energy $\hbar \omega$. The second condition $E_f = E_i + \hbar \omega$ (Absorption) shows that $E_f > E_i$. The system absorbs a photon of energy $\hbar \omega$ and ends up in an excited state of (higher) E_f energy as shown in Fig.(3.4). In conclusion, the effect of a harmonic perturbation is either absorption or emission. In sharp contrast, a constant (time independent) perturbation neither transfers energy to the system nor removes energy from it.

Remark

For transition into a continuum of final states, we can show, by analogy with the derivation of Eq.(3.14) Eq(3.20) leads to the absorption and emission transition rates.

$$W_{if}^{emi} = \frac{2\pi}{\hbar} |\langle \psi_f | \hat{v}^\dagger | \psi_i \rangle|^2 \rho(E_f) \Big|_{E_f=E_i-\hbar\omega}$$

$$\frac{W_{if}^{emi}}{\rho(E_f) \Big|_{E_f=E_i-\hbar\omega}} = \frac{2\pi}{\hbar} |\langle \psi_f | \hat{v}^\dagger | \psi_i \rangle|^2 \quad (3.21)$$

Similarly, the absorption rate

$$W_{if}^{abs} = \frac{2\pi}{\hbar} |\langle \psi_f | \hat{v} | \psi_i \rangle|^2 \rho(E_f) \Big|_{E_f=E_i+\hbar\omega}$$

$$\frac{W_{if}^{abs}}{\rho(E_f) \Big|_{E_f=E_i+\hbar\omega}} = \frac{2\pi}{\hbar} |\langle \psi_f | \hat{v} | \psi_i \rangle|^2$$

Since the perturbation is Hermitian, so

$$|\langle \psi_f | \hat{v} | \psi_i \rangle|^2 = |\langle \psi_f | \hat{v}^\dagger | \psi_i \rangle|^2$$

So Eq.(3.21) becomes

$$\frac{W_{if}^{emi}}{\rho(E_f) \Big|_{E_f=E_i-\hbar\omega}} = \frac{2\pi}{\hbar} |\langle \psi_f | \hat{v} | \psi_i \rangle|^2$$

Comparing both equations

$$\frac{W_{if}^{abs}}{\rho(E_f) \Big|_{E_f=E_i+\hbar\omega}} = \frac{W_{if}^{emi}}{\rho(E_f) \Big|_{E_f=E_i-\hbar\omega}}$$

This relation is known as the condition of detailed balancing.

3.4 Interaction of Atoms with Radiation

One of the most important application of time-dependent perturbation theory is to study the interaction of atomic electrons with an external electromagnetic radiation. By this

application we can find out structure of atoms. In the absence of an external perturbation (radiation), the Hamiltonian of atomic electron is

$$\hat{H}_0 = \frac{\vec{p}^2}{2m_e} + V_0(\vec{r})$$

Where, $\frac{p^2}{2m_e}$ is the kinetic energy, m_e is the mass of electron, $V_0(\vec{r})$ = Potential energy due to interaction of electron with the other electron and nucleus.

If the electromagnetic radiation of vector field $\vec{A}(\vec{r}, t)$ and scalar field $\varphi(\vec{r}, t)$ is applied on the atom, the total Hamiltonian will become

$$\hat{H} = \hat{H}_0 + \hat{H}_r + \hat{V}(t) \quad (3.22)$$

H_r is the Hamiltonian of the electromagnetic field, $\hat{V}(t)$ = interaction between electron and radiation.

$$\hat{V}(t) = \frac{e}{m_e c} \vec{A}(\vec{r}, t) \cdot \vec{p} \quad (3.23)$$

$\hat{H}_r + \hat{V}(t)$ is very small as compared to $\hat{H}_0$. $\hat{V}(t)$ is same as we studied in Harmonic perturbation,

$$\hat{V}(t) = \hat{v}e^{-i\omega t} + \hat{v}^\dagger e^{+i\omega t} \quad (3.24)$$

The first part of the Eq.(3.24) represents the absorption and second part of Eq.(3.24) represents the emission. To obtain the form of Eq.(3.23) in harmonic perturbation, we find out $\vec{A}(\vec{r}, t)$ by classical approach as well as quantum approach.

Classical Treatment of Incident Radiation

In classical treatment, incident radiation is valid only when large number of photons (having large intensity) are interacting with atom. Classically, we deal the various fields (such as $\vec{E}, \vec{B}, \vec{A}$) as vectors. So,

$$\vec{A}(\vec{r}, t) = \sqrt{\frac{2\pi\hbar c^2}{\omega V}} \left[e^{i(\vec{k} \cdot \vec{r} - \omega t)} + e^{-i(\vec{k} \cdot \vec{r} - \omega t)} \right] \cdot \hat{\epsilon}, \quad (3.25)$$

where, $\hat{\epsilon}$ is the polarization vector, $\hbar\omega$ is the energy of photon, V is the volume in which single photon lie. By putting in Eq.(3.23), we get

$$\hat{V}(t) = \frac{e}{m_e c} \left(\frac{2\pi\hbar c^2}{\omega V} \right)^{1/2} \hat{\epsilon} \cdot \vec{p} \left[e^{i(\vec{k} \cdot \vec{r} - \omega t)} + e^{-i(\vec{k} \cdot \vec{r} - \omega t)} \right] \quad (3.26)$$

This shape is similar to Eq.(3.24) of harmonic perturbation,

$$\hat{V}(t) = \hat{v} e^{-i\omega t} + \hat{v}^\dagger e^{i\omega t} \quad (3.27)$$

$$v = \frac{e}{m_e} \left(\frac{2\pi\hbar}{\omega V} \right)^{1/2} \hat{\epsilon} \cdot \vec{P} e^{i(\vec{k} \cdot \vec{r})}$$

This equation shows the absorption of radiation.

$$\hat{v}^\dagger = \frac{e}{m_e} \left(\frac{2\pi\hbar}{\omega V} \right)^{1/2} \hat{\epsilon} \cdot \vec{P} e^{-i(\vec{k} \cdot \vec{r})}$$

This equation shows the emission of radiation. The factor $\frac{e}{m_e} \left(\frac{2\pi\hbar}{\omega V} \right)^{1/2}$ represents the strength of radiation field. The factor $\hat{\epsilon} \cdot \vec{P}$ represents the polarization of the plane wave and the factor $e^{-i(\vec{k} \cdot \vec{r})}$ represents the propagation of plane wave.

Eq.(3.26) represents the stimulated emission and absorption. In stimulated emission, we start with one incident photon and end up with two: incident photon plus photon given by the atom resulting from transition to lower energy level. If we have a large number of atoms in the same excited state, the incident photon interacts with the first atom, it will produce two photons, which in turn produce four photons. These four photons then produce eight photons and so on.

Two such radiation amplification have been achieved experimentally and having many applications.

1. Microwave; MASER (Microwave amplification by stimulated emission of radiation).

2. Light wave; LASER (Light amplification by stimulated emission of radiation).

Put Eq.(3.26) in the transition rates, we have

$$\Gamma_{if} = \frac{2\pi}{\hbar} |\langle \psi_f | v | \psi_i \rangle|^2 \delta[E_f - E_i - \hbar\omega] + \frac{2\pi}{\hbar} |\langle \psi_f | v^\dagger | \psi_i \rangle|^2 \delta[E_f - E_i + \hbar\omega]$$

The first term in the above equation shows the absorption and second term shows the emission, which are written separately after putting the values of v and $v^\dagger$.

$$\Gamma_{if}^{abs} = \frac{4\pi^2 e^2}{m_e^2 \omega V} \left| \langle \psi_f | e^{i(\vec{k} \cdot \vec{r})} \hat{\epsilon} \cdot \vec{P} | \psi_i \rangle \right|^2 \delta[E_f - E_i - \hbar\omega] \quad (3.28)$$

and

$$\Gamma_{if}^{emi} = \frac{4\pi^2 e^2}{m_e^2 \omega V} \left| \langle \psi_f | e^{-i(\vec{k} \cdot \vec{r})} \hat{\epsilon} \cdot \vec{P} | \psi_i \rangle \right|^2 \delta[E_f - E_i + \hbar\omega] \quad (3.29)$$

These are the classical relation for transition rates. If $A = 0$ (no radiation fall on atom), so

$$\Gamma_{if}^{abs} = \Gamma_{if}^{emi} = 0 \quad (3.30)$$

So, classically we can not explain the spontaneous emission. This is explained only by quantum mechanics.

Quantum Treatment of Incident Radiation

In quantum treatment, only a finite number of photons (having small intensity) are involved. For quantum description of radiation, we replace the various fields ($\vec{E}, \vec{B}, \vec{A}(r, t)$) with operators. In the absence of charge (q) and current (I), $\vec{E}$ and $\vec{B}$ depends only on $\vec{A}(r, t)$. Here electromagnetic wave has two polarization vectors ϵ_1 and ϵ_2 as shown in Fig. (3.5).

The quantization of radiation is achieved by writing the electromagnetic field (wave) in term of creation (Raising $a^\dagger$) and annihilation (lowering a) operators as we did in classical harmonic oscillator.

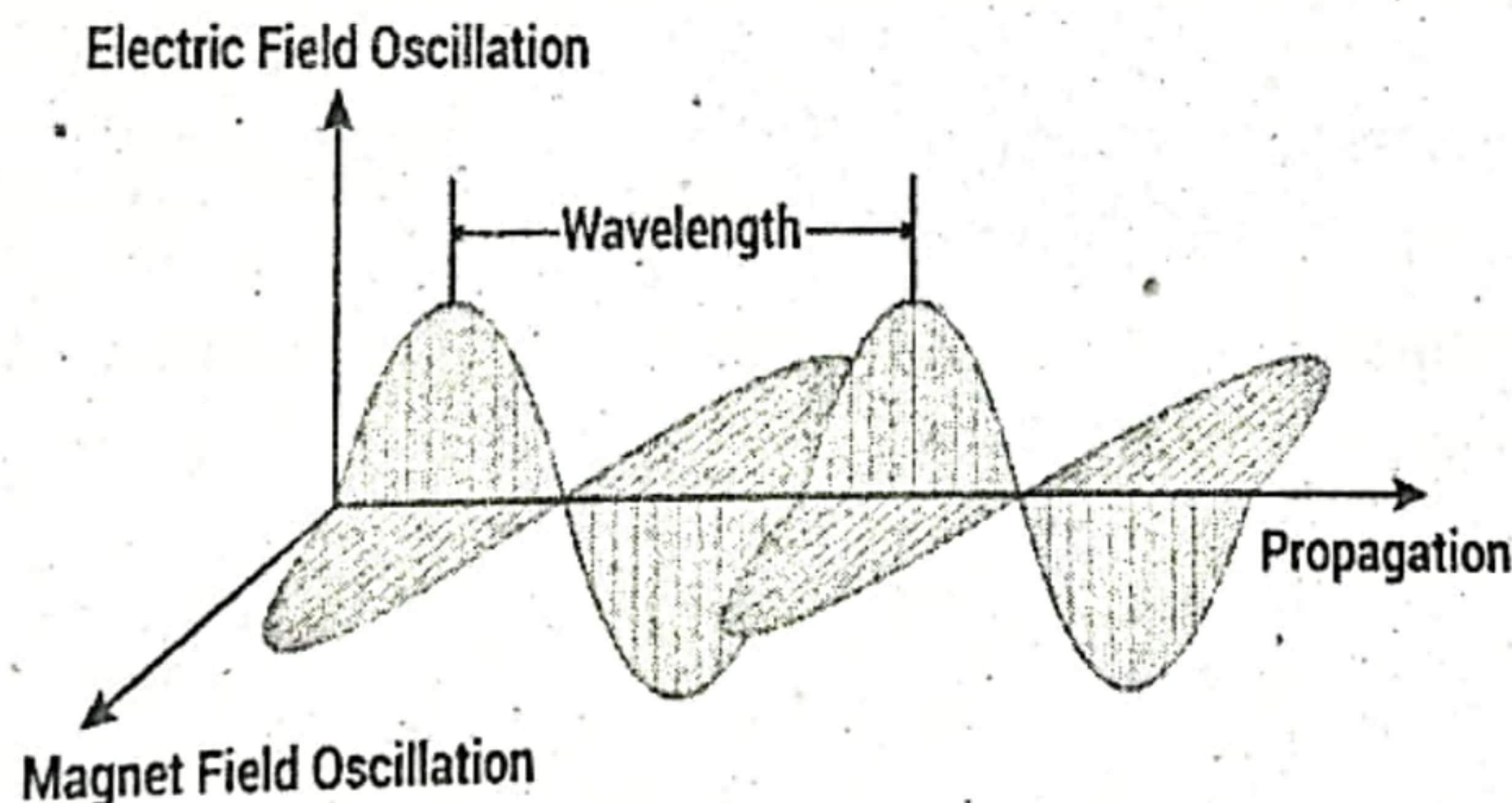


Fig. 3.5. Propagation of electromagnetic waves.

This process is called second quantization.

$$a |n\rangle = \sqrt{n} |n-1\rangle, a^\dagger |n\rangle = \sqrt{(n+1)} |n+1\rangle$$

Now the quantum relation for $\hat{A}$,

$$\hat{A}_{\lambda,k}(\vec{r}, t) = \sum_k \sum_{\lambda=1}^2 \sqrt{\frac{2\pi\hbar c^2}{\omega_k V}} \left[a_{\lambda,k} e^{i(k \cdot \vec{r} - \omega_k t)} \epsilon_{\lambda} + a_{\lambda,k}^{\dagger} e^{-i(k \cdot \vec{r} - \omega_k t)} \epsilon_{\lambda}^* \right]$$

Where, $\vec{k}$ is the wave vector; $k = \frac{2\pi}{\lambda}$, λ is the polarization which has two values. Put this in Eq. (3.23), we get

$$\begin{aligned} \hat{V}(t) &= \frac{e}{m_e c} \hat{A}_{\lambda,k}(\vec{r}, t) \cdot \vec{P} \\ \hat{V}(t) &= \frac{e}{m_e} \sum_k \sum_{\lambda} \sqrt{\frac{2\pi\hbar}{\omega_k V}} \left[a_{\lambda,k} e^{ik \cdot \vec{r}} \epsilon_{\lambda} \cdot \vec{P} e^{-i\omega_k t} + a_{\lambda,k}^{\dagger} e^{-ik \cdot \vec{r}} \epsilon_{\lambda}^* \cdot \vec{P} e^{i\omega_k t} \right] \end{aligned}$$

Now, this is the form of harmonic perturbation

$$\hat{V}(t) = \sum_k \sum_{\lambda=1}^2 \left[v e^{-i\omega_k t} + v^{\dagger} e^{i\omega_k t} \right]$$

$$v = \frac{e}{m_e} \sqrt{\frac{2\pi\hbar}{\omega_k V}} a e^{i\vec{k} \cdot \vec{r}} \epsilon_{\lambda} \cdot \vec{P}$$

$$v^{\dagger} = \frac{e}{m_e} \sqrt{\frac{2\pi\hbar}{\omega_k V}} a^{\dagger} e^{-i\vec{k} \cdot \vec{r}} \epsilon_{\lambda}^* \cdot \vec{P}$$

Before the atom and radiation interaction, the initial state is

$$|\varphi_i\rangle = |\psi_i\rangle |n\rangle_i$$

$|\psi_i\rangle$ is the un-perturbed state of atom, $|n\rangle_i$ is the state of radiation. After the atom and radiation interaction, the final state is

$$|\varphi_f\rangle = |\psi_f\rangle |n\rangle_f$$

In case of emission state changes from $|\varphi_i\rangle$ to $|\varphi_f\rangle = |\psi_f\rangle |n+1\rangle_f$ by applying $v^{\dagger}$ or $a^{\dagger}$ on state $|n\rangle_i$.

$$\begin{aligned}
 \langle \varphi_f | v^\dagger | \varphi_i \rangle &= \langle \psi_f | \langle n+1 |_f \frac{e}{m_e} \sqrt{\frac{2\pi\hbar}{\omega V}} a^\dagger e^{-i\vec{k}\cdot\vec{r}} \vec{\epsilon}_\lambda^* \cdot \vec{P} | \psi_i \rangle | n \rangle_i \\
 &= \frac{e}{m_e} \sqrt{\frac{2\pi\hbar}{\omega V}} \langle \psi_f | e^{-i\vec{k}\cdot\vec{r}} \vec{\epsilon}_\lambda^* \cdot \vec{P} | \psi_i \rangle \langle n+1 | a^\dagger | n \rangle \\
 &= \frac{e}{m_e} \sqrt{\frac{2\pi\hbar}{\omega V}} \sqrt{n+1} \langle \psi_f | e^{-i\vec{k}\cdot\vec{r}} \vec{\epsilon}_\lambda^* \cdot \vec{P} | \psi_i \rangle \langle n+1 | n+1 \rangle \\
 &= \frac{e}{m_e} \sqrt{\frac{2\pi\hbar}{\omega V}} \sqrt{n+1} \langle \psi_f | e^{-i\vec{k}\cdot\vec{r}} \vec{\epsilon}_\lambda^* \cdot \vec{P} | \psi_i \rangle
 \end{aligned} \tag{3.31}$$

This is the relation for stimulated emission ($n \neq 0$) and spontaneous emission ($n = 0$). In case of absorption state changes from $|\varphi_i\rangle$ to $|\varphi_f\rangle = |\psi_f\rangle |n-1\rangle_f$ by applying v or a on state $|n\rangle_i$

$$\begin{aligned}
 \langle \varphi_f | v | \varphi_i \rangle &= \langle \psi_f | \langle n-1 |_f \frac{e}{m_e} \sqrt{\frac{2\pi\hbar}{\omega V}} a e^{i\vec{k}\cdot\vec{r}} \vec{\epsilon}_\lambda \cdot \vec{P} | \psi_i \rangle | n \rangle_i \\
 &= \frac{e}{m_e} \sqrt{\frac{2\pi\hbar}{\omega V}} \sqrt{n} \langle \psi_f | e^{i\vec{k}\cdot\vec{r}} \vec{\epsilon}_\lambda \cdot \vec{P} | \psi_i \rangle
 \end{aligned}$$

Now the transition rates will become

$$\Gamma_{if}^{emi} = \frac{2\pi}{\hbar} |\langle \psi_f | v^\dagger | \psi_i \rangle|^2 \delta[E_f - E_i + \hbar\omega]$$

Using Eq.(3.31),

$$= \frac{4\pi^2 e^2}{m_e^2 \omega V} (n+1) |\langle \psi_f | e^{-i\vec{k}\cdot\vec{r}} \vec{\epsilon}_\lambda^* \cdot \vec{P} | \psi_i \rangle|^2 \delta[E_f - E_i + \hbar\omega]$$

Similarly,

$$\begin{aligned}
 \Gamma_{if}^{Abs.} &= \frac{2\pi}{\hbar} |\langle \psi_f | v | \psi_i \rangle|^2 \delta[E_f - E_i - \hbar\omega] \\
 &= \frac{4\pi^2 e^2}{m_e^2 \omega V} (n) |\langle \psi_f | e^{i\vec{k}\cdot\vec{r}} \vec{\epsilon}_\lambda \cdot \vec{P} | \psi_i \rangle|^2 \delta[E_f - E_i - \hbar\omega]
 \end{aligned}$$

These are the required results.

3.5 Selection Rules For Electric Dipole: (Allowed) Electron Transitions

To derive the selection rules for spontaneous emission, we use the systems like hydrogen, for which the Hamiltonian is spherically symmetric. In that case we may specify the states with the usual quantum numbers³ n, l, m_l, m_s .

$$\psi_i = n, l, m_l$$

$$\psi_f = n', l', m'_l$$

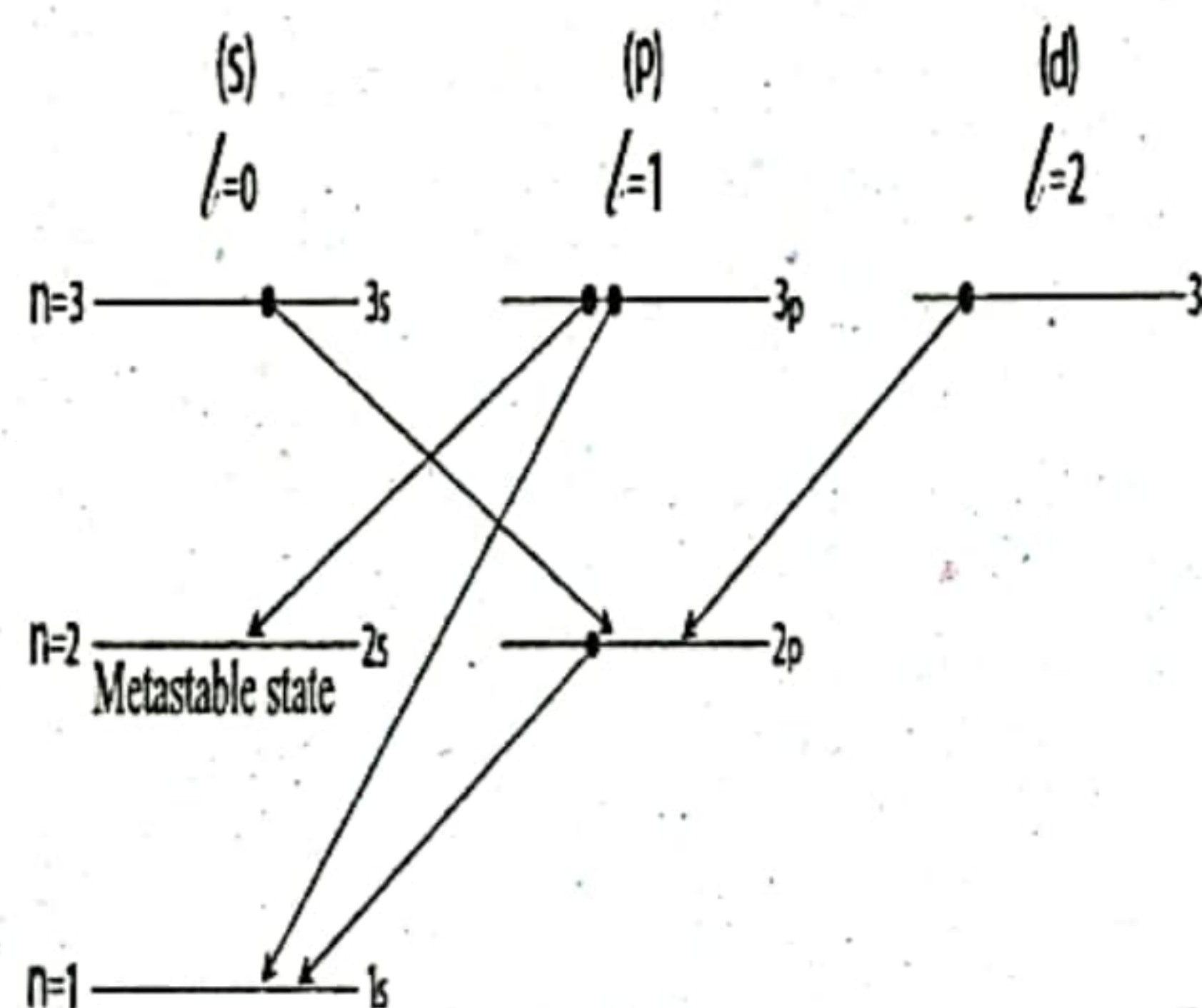


Fig. 3.6. The scheme of allowed transitions for first three Bohr's levels in hydrogen atom.

There are two selection rules:

1. Selection rule involving m and m' . No transition occur unless

$$\Delta m = 0, \pm 1 \quad (3.32)$$

2. Selection rule involving l and l' . No transition occur unless

$$\Delta l = \pm 1 \quad (3.33)$$

³ $m_l = 2l + 1$; $l = 0, 1, \dots, n - 1$

Evidently not all transitions to lower energy states can proceed by spontaneous emission; some are forbidden by the selection rules. The scheme of allowed transitions for first three Bohr's levels in hydrogen is shown in Fig. (3.6).

Note that the $2s$ (state) $\psi_{200} = \psi_{nlm}$ is stuck. It can not decay because there is no lower energy state. So it is called meta-stable state and its life time is much longer than $2p$. ($\psi_{21-1}, \psi_{210}, \psi_{211}$). Metastable states do eventually decay, either by collision or by multi-photon emission.

3.6 Spin of Photon and its Helicity

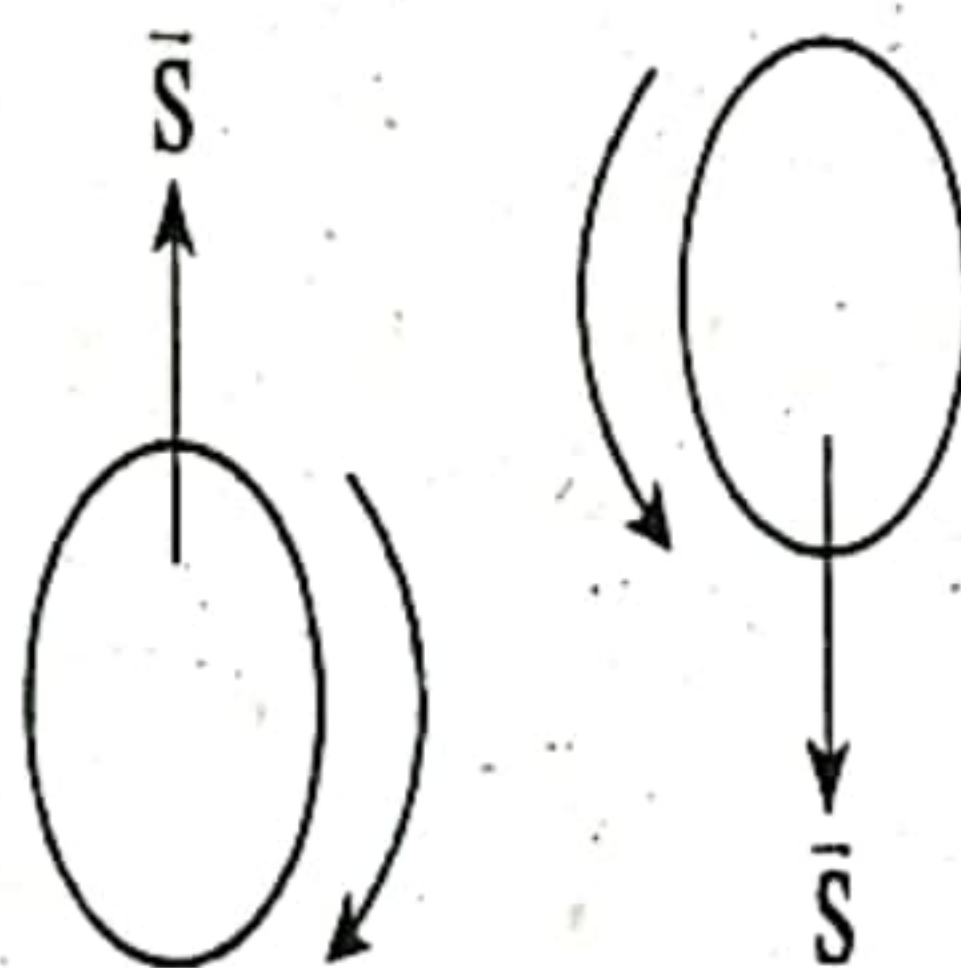


Fig. 3.7. Schematic picture spin in clockwise and anti-clockwise direction.

A photon is a type of elementary particle, quantum (packet) of electromagnetic field including the electromagnetic radiation such as light. The photon has zero rest mass and always moves at the speed of light within a vacuum. It has spin ± 1 . Thus its helicity must be $\pm \hbar$.

Helicity is the projection of spin $\vec{s}$ onto the direction of linear momentum $\vec{P}$.

Helicity states are very useful in the context of general collision problems. Pseudo-scalar operator, $\Lambda = \vec{s} \cdot \vec{p} / |\vec{p}|$. Helicity is the eigenvalue of this operator.

3.7 Review Questions

- 3.1 Why transition probability at $\omega_{fi} = \omega$ act as absorption for harmonic perturbation?
- 3.2 Why energy is conserved in $\delta(E_f - E_i)$ in constant perturbation?
- 3.3 What is the time period of transition probability of oscillating sinusoidal function?
- 3.4 When the transition probability is delta function?
- 3.5 Why absorption and emission process cannot occur simultaneously?
- 3.6 Write two necessary conditions for the existence of P_{if} for a harmonic perturbation.
- 3.7 Why transition probability has an interference pattern?
- 3.8 Define MASER and LASER.
- 3.9 Define selection rules for transition.
- 3.10 Define helicity of spin.



3.8 Solved Problems

- 3.1. A system in an unperturbed state n is suddenly subjected to a constant perturbation $H'(r)$ which exists during time $0 \rightarrow t$. Find the probability for transition from state n to state k and show that it varies simple harmonically with angular frequency $\frac{(E_k - E_n)}{2\hbar}$ and amplitude $\frac{4|H'_{kn}|^2}{(E_k - E_n)^2}$.

Solution

Equation $C_k^{(1)}(t) = \frac{1}{i\hbar} \int_0^t H'_{kn}(r, t') \exp(i\omega_{kn}t') dt'$ gives the value of $C_k^{(1)}(t)$. When the perturbation is constant in time, $H'_{kn}(r)$ can be taken outside the integral. Hence,

$$\begin{aligned} C_k^{(1)}(t) &= \frac{H'_{kn}(r)}{i\hbar} \int_0^t \exp(i\omega_{kn}t') dt' \\ &= -\frac{H'_{kn}}{\hbar\omega_{kn}} [\exp(i\omega_{kn}t) - 1] \end{aligned}$$

$$\begin{aligned}
 &= -\frac{H'_{kn}}{\hbar\omega_{kn}} \exp(i\omega_{kn}t/2) [\exp(i\omega_{kn}t/2) - \exp(-i\omega_{kn}t/2)] \\
 &= -\frac{2iH'_{kn}}{\hbar\omega_{kn}} \exp(i\omega_{kn}t/2) \sin(\omega_{kn}t/2) \\
 |C_k^{(1)}(t)|^2 &= \frac{4}{\hbar^2} \frac{|H'_{kn}|^2}{\omega_{kn}^2} \sin^2(\omega_{kn}t/2)
 \end{aligned}$$

Which is the probability for transition from state n to state k . From the above expression it is obvious that the probability varies simple harmonically with angular frequency $\frac{\omega_{kn}}{2} = \frac{(E_k - E_n)}{2\hbar}$. The amplitude of vibration is $\frac{4|H'_{kn}|^2}{\hbar^2\omega_{kn}^2} = \frac{4|H'_{kn}|^2}{(E_k - E_n)^2}$.



3.2. Spontaneous emission for exceeds stimulated emission in the visible region, whereas reverse the situation in the microwave region.

Solution

Visible region Wavelength $\approx 5000\text{\AA}$. So, Rate of spontaneous emission / Rate of stimulated emission $= e^{\frac{h\nu}{kT}} - 1$.

$$\begin{aligned}
 \frac{h\nu}{kT} &= \frac{hc}{\lambda kT} \\
 &= \frac{(6.63 \times 10^{-34} \text{ Js}) (3 \times 10^8 \text{ ms}^{-1})}{(5000 \times 10^{-10} \text{ m}) (1.38 \times 10^{-23} \text{ JK}^{-1}) 300 \text{ K}} \\
 &= 96.03
 \end{aligned}$$

The rate of spontaneous emission $= (e^{96.03} - 1) \times \text{rate of stimulated emission}$
 $= 4.073 \times \text{rate of stimulated emission}$

Microwave region: Wavelength $\cong 1\text{cm}$. Therefore,

$$\begin{aligned}
 \frac{h\nu}{kT} &= \frac{hc}{\lambda kT} \\
 &= \frac{(6.63 \times 10^{-34} \text{ Js}) (3 \times 10^8 \text{ ms}^{-1})}{(0.01 \text{ m}) (1.38 \times 10^{-23} \text{ JK}^{-1}) 300 \text{ K}} \\
 &= 0.004
 \end{aligned}$$

The rate of spontaneous emission $= (e^{0.004} - 1) \times \text{rate of stimulated emission}$

$$= 0.004 \times \text{rate of stimulated emission.}$$

Hence the required result.



3.3. Prove the following:

I: If the source temperature is 1000K, in the optical region ($\lambda = 5000\text{\AA}$), the emission is predominantly due to spontaneous transitions.

II: If the source temperature is 300K, in the microwave region ($\lambda = 1\text{cm}$), the emission is predominantly due to stimulated transitions. The Boltzmann constant is $1.38 \times 10^{-23} \text{ JK}^{-1}$.

Solution

$$\text{Spontaneous emission rate/Stimulated emission rate} = \exp\left(\frac{h\nu}{kT}\right) - 1$$

I: In the optical region,

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^8}{5000 \times 10^{-10}} = 6 \times 10^{14} \text{ Hz}$$

$$\frac{h\nu}{kT} = \frac{6.63 \times 10^{-34} \times 6 \times 10^{14}}{1.38 \times 10^{-23} \times 1000} = 28.8$$

$$\exp(28.8) - 1 = 3.22 \times 10^{12}$$

Thus, the spontaneous emission is predominant.

II. In the microwave region,

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^8}{10^{-2}} = 3 \times 10^{10} \text{ Hz}$$

$$\frac{h\nu}{kT} = \frac{6.63 \times 10^{-34} \times 3 \times 10^{10}}{1.38 \times 10^{-23} \times 300} = 4.8 \times 10^{-3}$$

$$\exp(4.8 \times 10^{-3}) - 1 = 0.0048.$$

Therefore, the stimulated emission is predominant.



3.4. The time varying Hamiltonian $H'(t)$ induces transitions between states $|j\rangle$ and $|k\rangle$. Using time-dependent perturbation theory, show that the probability for a transition from state $|j\rangle$ to state $|k\rangle$ is the same as the probability for a transition from state $|k\rangle$ to state $|j\rangle$.

Solution

The probability for a transition from state $|j\rangle$ to state $|k\rangle$ at time t is $P_{j \rightarrow k}(t) = |C_{j \rightarrow k}(t)|^2$. The relation for $C_{j \rightarrow k}$ is

$$C_{j \rightarrow k}(t) = \frac{1}{i\hbar} \int_0^t \langle k | H' | j \rangle \exp(i\omega_{kj}t) dt$$

See the equation becomes

$$C_k^{(1)}(t) = \frac{1}{i\hbar} \int_0^t H'_{kn}(r, t') \exp(i\omega_{kn}t') dt'$$

The coefficient for transition from state $|k\rangle$ to state $|j\rangle$ is given by

$$C_{k \rightarrow j}(t) = \frac{1}{i\hbar} \int_0^t \langle j | H' | k \rangle \exp(i\omega_{jk}t) dt$$

Since H' is Hermitian, $\langle k | H' | j \rangle = \langle j | H' | k \rangle$. Also, it follows that $\hbar\omega_{kj} = E_k - E_j = -\hbar\omega_{jk}$. As the integrand of the second integral is the complex conjugate of that of the first one, we have

$$|C_{j \rightarrow k}(t)|^2 = |C_{k \rightarrow j}(t)|^2$$

$$P_{j \rightarrow k}(t) = P_{k \rightarrow j}(t)$$



3.5. A quantum mechanical system is initially in the ground state $|0\rangle$. At $t=0$, a perturbation of the form $H'(t) = H_0 e^{-\alpha t}$, where α is a constant, is applied. Show that the probability that the system is in state $|1\rangle$ after long time is $P_{10} = \frac{|\langle 0 | H_0 | 1 \rangle|^2}{\hbar^2(\alpha^2 + \omega_{10})^2}$, $\omega_{10} = \frac{E_1 - E_0}{\hbar}$.

Solution

In the first order perturbation, the transition probability amplitude is given by equation so,

$$C_k^{(1)}(t) = \frac{1}{i\hbar} \int_0^t H'_{kn} \exp(i\omega_{kn}t') dt'$$

where,

$$H'_{kn} = \langle k | H' | n \rangle, \omega_{kn} = \frac{E_k - E_n}{\hbar}$$

Substituting the value of H' and allowing $t \rightarrow \infty$, we get

$$\begin{aligned} C_k^{(1)}(t) &= \frac{1}{i\hbar} \int_0^\infty \exp(i\omega_{10}t) e^{-\alpha t} \langle 1 | H_0 | 0 \rangle dt \\ &= \frac{\langle 1 | H_0 | 0 \rangle}{i\hbar} \left[\frac{\exp[-(\alpha - i\omega_{10})t]}{-(\alpha - i\omega_{10})} \right]_0^\infty \\ &= \frac{\langle 1 | H_0 | 0 \rangle}{i\hbar} \frac{1}{\alpha - i\omega_{10}} \end{aligned}$$

The probability for a transition from state $|0\rangle$ to a state $|1\rangle$ after a long time is

$$P_{10} = |C_k^{(1)}|^2 \frac{|\langle 0 | H_0 | 1 \rangle|^2}{\hbar^2(\alpha^2 + \omega_{10}^2)^2}$$



3.9 Multiple Choice Questions

- Height of central peak in probability is proportional to :
a) $\frac{1}{t}$ b) t^2 c) t d) None
- $\omega_{fi} = 0$ is maximum when
a) $E_f - E_i$ b) $E_f > E_i$ c) $E_f < E_i$ d) $E_f \neq E_i$
- The transition probability exhibits a pattern like
a) Scattering b) Interference c) Straight d) None of these
- The transition rate exists for constant perturbation when the energy is
a) Conserved b) Non-conserved c) Zero d) None
- Transition probability of harmonic perturbation will be maximum when ω_{fi} is equal to
a) $+\omega$ b) $-\omega$ c) $\pm\omega$ d) $\omega = 0$
- Probability at constant perturbation is
a) $\omega_{fi} = 0$ b) $\omega_{fi} = 1$ c) $\omega_{fi} = \frac{1}{2}$ d) None of these
- We attain delta function when time is
a) $t = 0$ b) $t > 0$ c) $t < 0$ d) $t \rightarrow \infty$
- Quantization of radiation is achieved by which operators
a) Raising b) Lowering c) Ladder d) Hamiltonian
- No electronic transition will occur unless
a) $\Delta m = 0, \pm 1$ b) $\Delta m = 0$ c) $\Delta m = \pm 1$ d) None of these
- The spin helicity of a photon is
a) $\hbar$ b) $\pm\hbar$ c) Both (a) and (b) d) None of these

Answers

1	b	2	a	3	b	4	a	5	c
6	a	7	d	8	c	9	a	10	b

Chapter 4

Scattering Theory

Scattering is a physical process in which light or particles are deflected by some target. Much of our understanding about the structure of matter is extracted by the scattering of known particles from the matter. For example, the description of an atom as being comprised of a positively charged central area of radius $\cong 10^{-13}$ cm, with external electrons, is due to scattering experiments performed by E. Rutherford in 1911.

4.1 Classical Scattering Theory

Consider a particle (proton) is incident on scattering center (nucleus) as shown in Fig. (4.1).

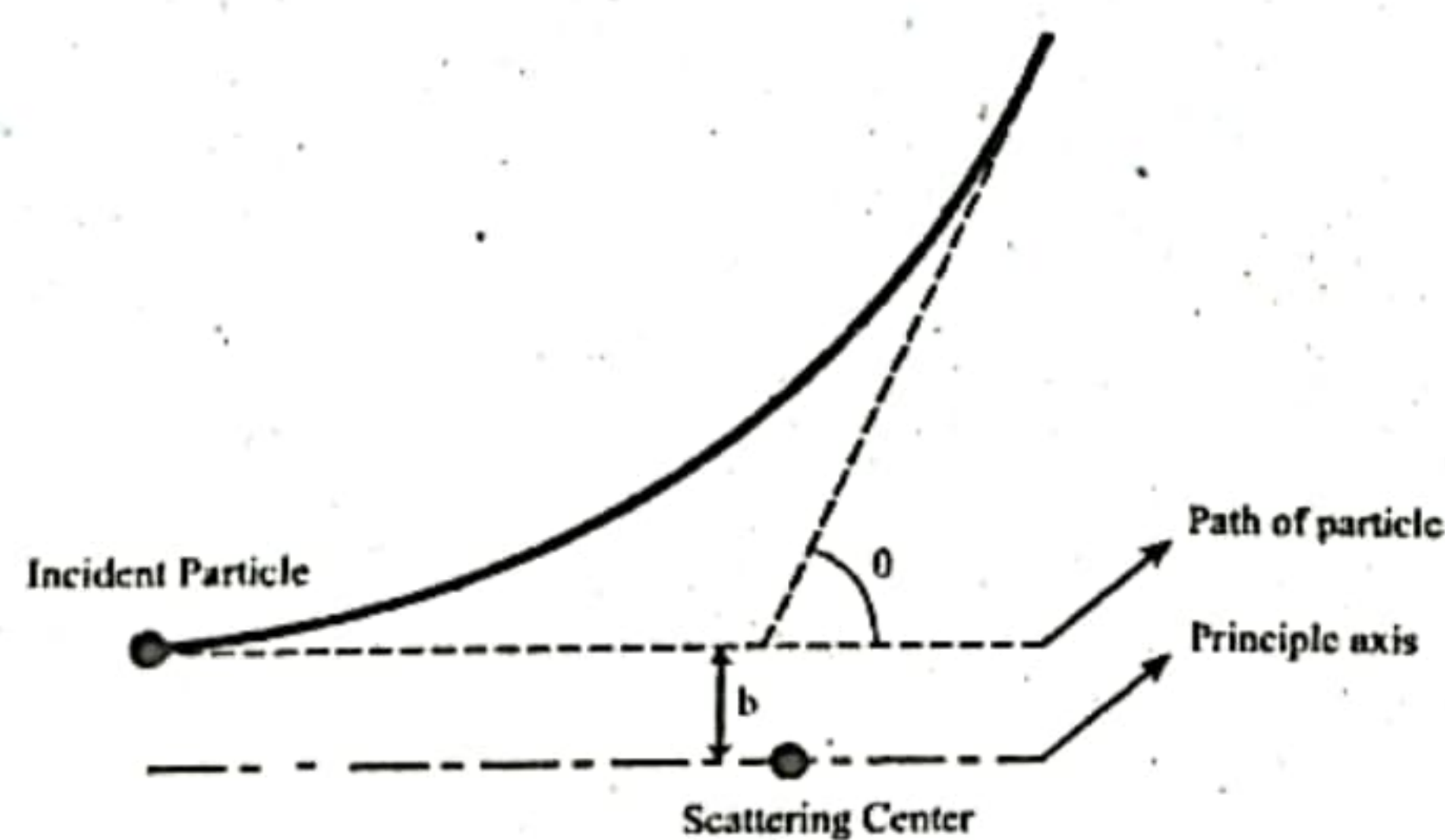


Fig. 4.1. The particle scattered by target having impact parameter b and the scattering angle θ .

The energy of incoming particle is E and impact parameter is b . Particle will scatter at angle θ . Assume for simplicity that the target is spherically symmetric, so the trajectory

of particle remains in one plane and the target is very heavy, so the recoil is negligible. If impact parameter ¹ b is small then scattering angle θ will be large. Particles incident within an infinitesimal patch of cross-sectional area $d\sigma$ will scatter into a corresponding infinitesimal solid angle $d\Omega$ (see Fig. (4.2)).

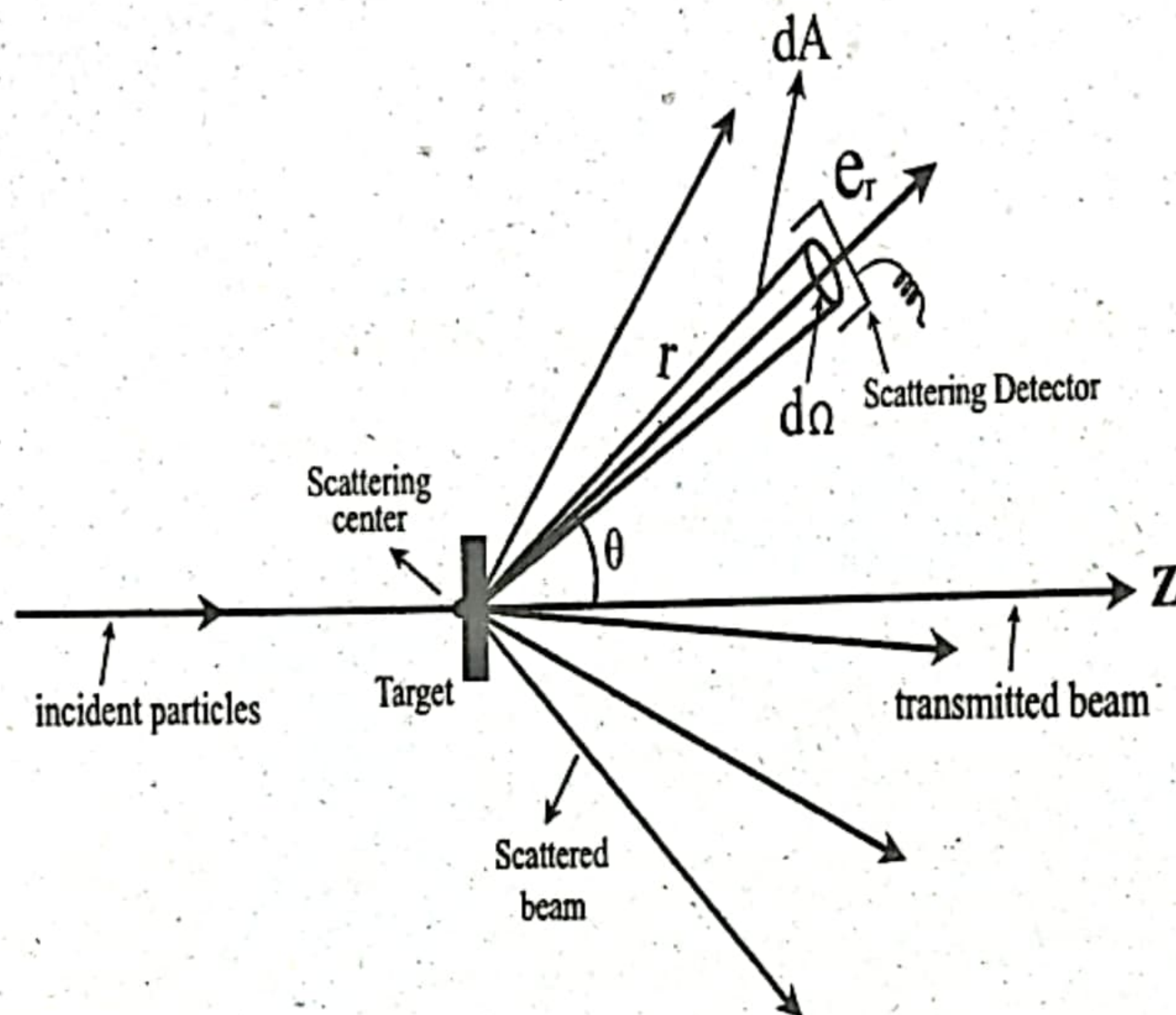


Fig. 4.2. Pictorial representation of scattering arrangement.

So, $d\sigma \propto d\Omega$. $d\Omega$ is the vector solid angle subtended by surface area dA about the target.

$$d\sigma = D(\theta) d\Omega$$

$$D(\theta) = \frac{d\sigma}{d\Omega} \quad (4.1)$$

$D(\theta)$ is differential (scattering) cross section. As dA is at a distance r from the target, so

$$dA = r^2 d\Omega$$

$$d\Omega = \frac{dA}{r^2}$$

In spherical coordinates $dA = r^2 \sin\theta d\theta d\phi$, $\theta = 0 \rightarrow \pi$ and $\phi = 0 \rightarrow 2\pi$. Thus, above equation becomes

¹ Impact parameter is defined as the distance between the incident particle and the target.

$$d\Omega = \frac{r^2 \sin\theta d\theta d\phi}{r^2}$$

$$\boxed{d\Omega = \sin\theta d\theta d\phi} \quad (4.2)$$

From Eq.(4.1),

$$d\sigma = D(\theta) d\Omega$$

Interestingly,

$$\int d\sigma = \int D(\theta) d\Omega$$

$$\boxed{\sigma = \int D(\theta) d\Omega} \quad (4.3)$$

The total scattering cross section is the integral of $D(\theta)$ over all solid angles. Roughly speaking, it is the total area of incident beam that is scattered by the target. Classically, the total cross section seen by a uniform beam of point particles incident on a fixed rigid sphere of radius R is

$$\boxed{\sigma = \pi R^2} \quad (4.4)$$

Suppose, we have a beam of incident particles with uniform intensity (luminosity) J_{sc} and J_{in} show the number of scattered and incident particles per unit area per unit time, respectively. If N is the total number of particles and dN is the number of scattered particles passing through dA per second (number of particles entering area $d\sigma$ per second)

$$dN = J_{sc} dA = J_{in} d\sigma$$

From Eq.(4.1), $d\sigma = D(\theta) d\Omega$,

$$dN = J_{in} D(\theta) d\Omega$$

$$\boxed{D(\theta) = \frac{1}{J_{in}} \frac{dN}{d\Omega}}$$

This is the definition of the differential cross-section, because these quantities are easily measured in laboratory. If the detector accepts the particles scattering into solid angle $d\Omega$, then we simply count the number recorded per unit time, divided by $d\Omega$ and normalize to the luminosity of incident beam.

4.2 Quantum Scattering Theory

In quantum mechanics, consider an incident plane wave traveling in the z -direction, with wave function:

$$\psi_{inc}(z) = A e^{ikz}$$

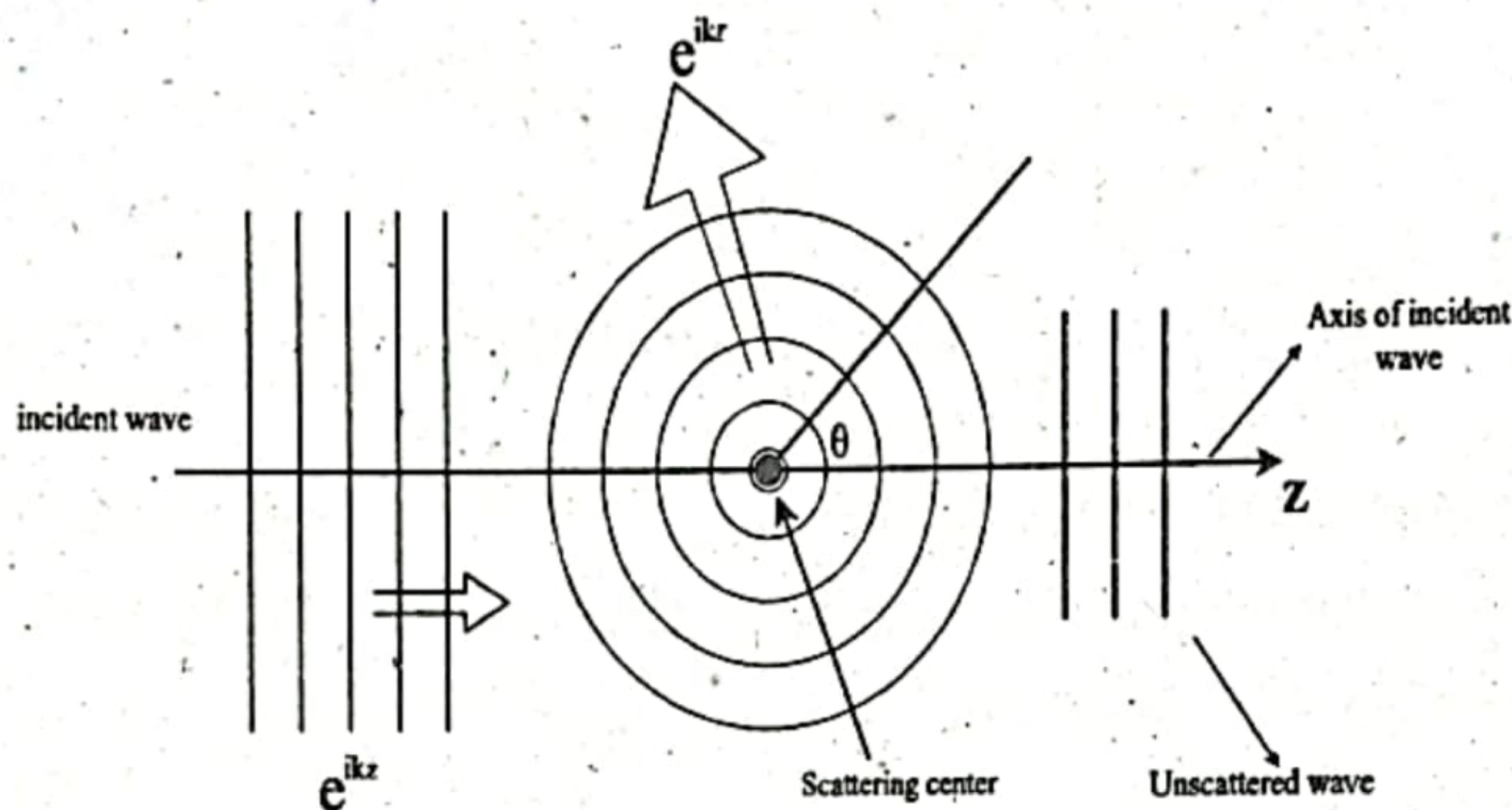


Fig. 4.3. Incoming plane wave produces outgoing spherical wave after scattering.

The plane wave then encounters a scattering potential, producing outgoing spherical waves as shown in Fig. (4.3). Scattering happens by interaction of fields of incoming wave and target object. Now the solution of the Schrödinger wave equation is the total wave consists of a superposition of the incident plane wave and the scattered wave.

$$\psi(r, \theta) = A \left[\underbrace{e^{ikz}}_{\text{incident}} + f(\theta) \underbrace{\frac{e^{ikr}}{r}}_{\text{scattered}} \right] \quad (r \rightarrow \infty) \quad (4.5)$$

Where k is the wave number, $k = \frac{2\pi}{\lambda}$, related to energy of the incident particles by

$$k = \frac{\sqrt{2mE}}{\hbar}$$

For elastic scattering, incident wave number k is equal to scattered wave number. Also, $f(\theta)$ is amplitude of the outgoing spherical wave depending on θ .

Our task is to calculate the scattering amplitude $f(\theta)$ which tells the probability of scattering in a given direction θ , and is related to the differential cross section $D(\theta)$.

Incident Probability

Consider the incident particle, moving with speed v passing through infinitesimal cross section area $d\sigma$ in time dt with wave function (see Fig.(4.4)a);

$$\psi_{\text{inc}}(z=) A e^{ikz}$$

Then the incident probability is,

$$dp_{\text{inc}} = |\psi_{\text{inc}}|^2 dV$$

$$dp_{\text{inc}} = \psi_{\text{inc}}^* \psi_{\text{inc}} dV \quad (4.6)$$

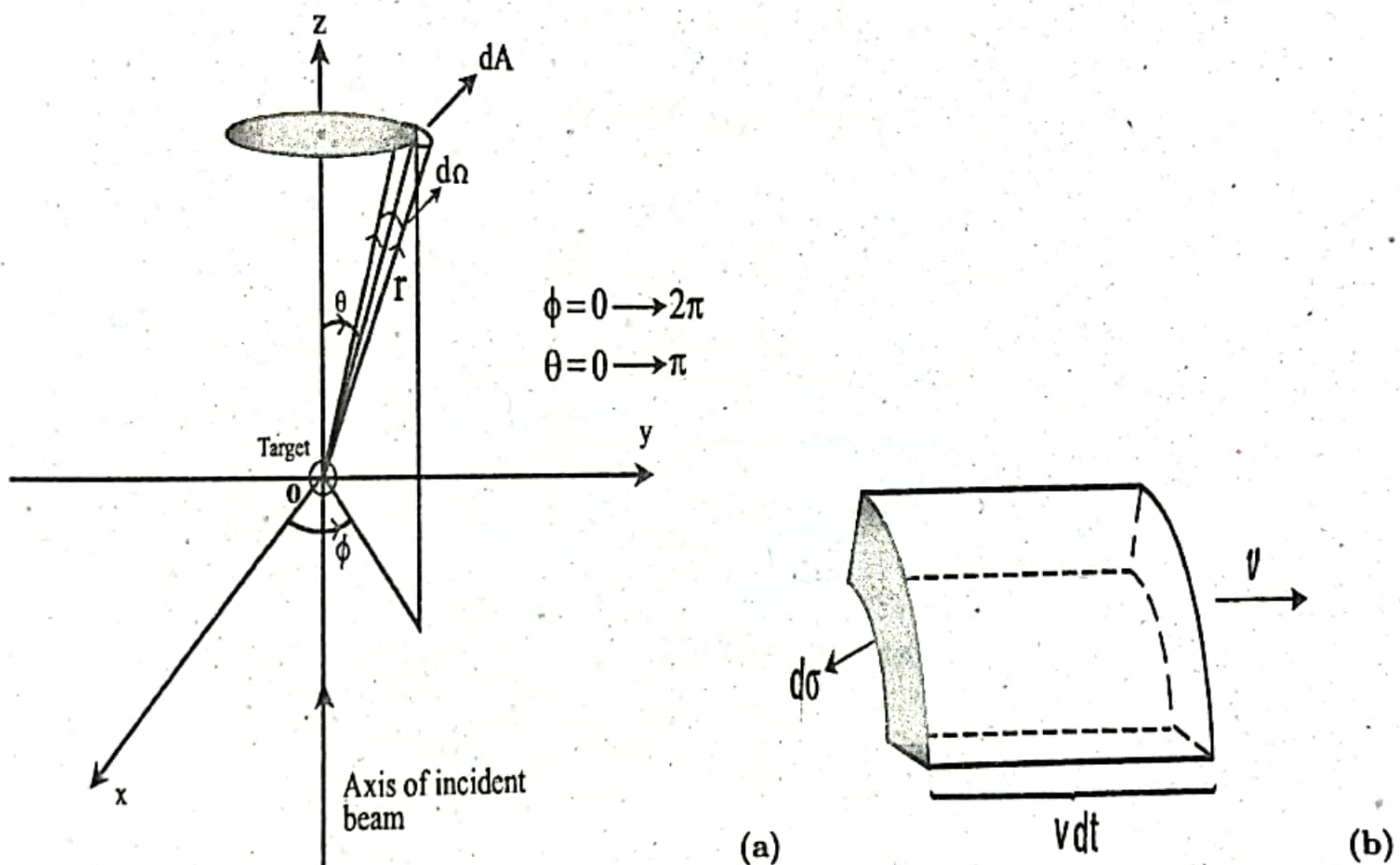


Fig. 4.4. (a) The scattering cross section is independent of the azimuthal angle ϕ for central potential of interaction $V(r)$. (b) The volume dV of incident beam that passes through area $d\sigma$ in time dt .

From Fig.(4.4)(b),

$$dV = (\text{Area}) (\text{Length})$$

$$dV (=d\sigma) v dt$$

Put this in Eq.(4.6),

$$dp_{\text{inc}} = A^* e^{-ikz} A e^{ikz} d\sigma v dt$$

$$\boxed{dp_{\text{inc}} = |A|^2 d\sigma v dt} \quad (4.7)$$

Scattering Probability

The scattering wave function is given by equation Eq.(4.5)

$$\psi_{\text{scat}} r = A f(\theta) \frac{e^{ikr}}{r}$$

Eq.(4.7) is equal to the scattering probability that the particle later emerges into the solid angle $d\Omega$.

$$dp_{\text{scat}} = |\psi_{\text{scat}}|^2 dV$$

$$dp_{\text{scat}} = \psi_{\text{scat}}^* \psi_{\text{scat}} dV$$

By putting values,

$$dp_{\text{scat}} = A^* f^*(\theta) \frac{e^{-ikr}}{r} A f(\theta) \frac{e^{ikr}}{r} dV$$

$$dp_{\text{scat}} = |A|^2 \frac{f^*(\theta) f(\theta)}{r^2} e^{-ikr} e^{ikr} dV$$

$$\boxed{dp_{\text{scat}} = \frac{|A|^2 |f(\theta)|^2}{r^2} dV} \quad (4.8)$$

Now again,

$$dV = (\text{Area}) (\text{Length})$$

where Area = $r^2 d\Omega$.

$$dV (= r^2 d\Omega) v dt \quad (4.9)$$

Eq. (4.8) becomes,

$$dp_{\text{scat}} = \frac{|A|^2 |f(\theta)|^2}{r^2} r^2 d\Omega v dt$$

$$\boxed{dp_{\text{scat}} = |A|^2 |f(\theta)|^2 v dt d\Omega} \quad (4.10)$$

which is the required scattering probability. As the incident probability must be equal to scattering probability.

$$dp_{\text{inc}} = dp_{\text{scat}}$$

Put the values from Eqs. (4.7) and (4.10),

$$|A|^2 d\sigma v dt = |A|^2 |f(\theta)|^2 v dt d\Omega$$

$$d\sigma = |f(\theta)|^2 d\Omega$$

$$\boxed{\frac{d\sigma}{d\Omega} = |f(\theta)|^2}$$

Moreover,

$$\boxed{\frac{d\sigma}{d\Omega} = D(\theta)}$$

Hence we see that, differential scattering cross-section is equal to absolute square of scattering wave amplitude $f(\theta)$. The total cross section is

$$\sigma = \int_{4\pi} |f(\theta)|^2 d\Omega = 2\pi \int_0^\pi |f(\theta)|^2 \sin\theta d\theta \quad \because d\Omega = \sin\theta d\theta d\phi$$

There are two methods for the calculation of $f(\theta)$.

(1) Partial Wave Analysis.

(2) Born Approximation.

4.3 Partial Waves Analysis

In partial wave analysis, we do not limitize the strength of scattering potential $V(\vec{r})$ and calculate the exact value of $f(\theta)$. In spherical polar co-ordinates, the solution of Schrödinger wave equation for a spherically symmetric potential $V(\vec{r})$ is given as:

$$\psi(r, \theta, \phi) = R(r) Y_l^m(\theta, \phi) \quad (4.11)$$

In Eq.(4.11), $Y_l^m(\theta, \phi)$ gives the spherical harmonic part and $U = rR(r)$ satisfies the radial equation.

$$-\frac{\hbar^2}{2m} \frac{d^2 U}{dr^2} + \left[V(r) + \frac{\hbar^2 l(l+1)}{2m r^2} \right] U = E U \quad (4.12)$$

where, l is azimuthal quantum number and U is wavefunction (like ψ .)

Radiation Zone ($kr \gg 1$)

If r increases, the potential becomes weak (i.e. $V(r) \rightarrow 0$) and the centrifugal term ($\frac{\hbar^2 l(l+1)}{2m r^2}$) is negligible. So,

$$\begin{aligned}\frac{d^2 U}{dr^2} &= -\frac{2mE}{\hbar^2} U \\ \frac{d^2 U}{dr^2} &= -k^2 U,\end{aligned}\quad (4.13)$$

where, $k^2 = \frac{2mE}{\hbar^2}$. Eq.(4.13) is the 2nd order homogenous differential equation and its solution is,

$$U(r) = \underbrace{C e^{ikr}}_{\text{outgoing}} + \underbrace{D e^{-ikr}}_{\text{incoming}} \quad (4.14)$$

Here, 1st term represents the outgoing spherical wave and 2nd term represents the incoming wave which is not possible i.e. $D \rightarrow 0$. So, Eq.(4.14) will give the acceptable solution for $U(r)$ at very large r ($kr \gg 1$)

$$U(r) \approx C e^{ikr}$$

Since, C calculated by condition of normalization, which is very small, so neglected.

$$U(r) \approx e^{ikr}$$

Then,

$$R(r) \approx \frac{e^{ikr}}{r} \quad (4.15)$$

This relation holds for radiation zone (i.e. $kr \gg 1$) (see Fig. (4.5)).

Intermediate Region ($V = 0$)

Now, in the intermediate region, where r is large then $V(r)$ can be neglected but centrifugal term will not approach to zero. Eq.(4.12) will become,

$$\begin{aligned}\frac{d^2 U}{dr^2} - \frac{l(l+1)}{r^2} U &= -\frac{2mE}{\hbar^2} U \\ \frac{d^2 U}{dr^2} - \frac{l(l+1)}{r^2} U &= -k^2 U\end{aligned}$$

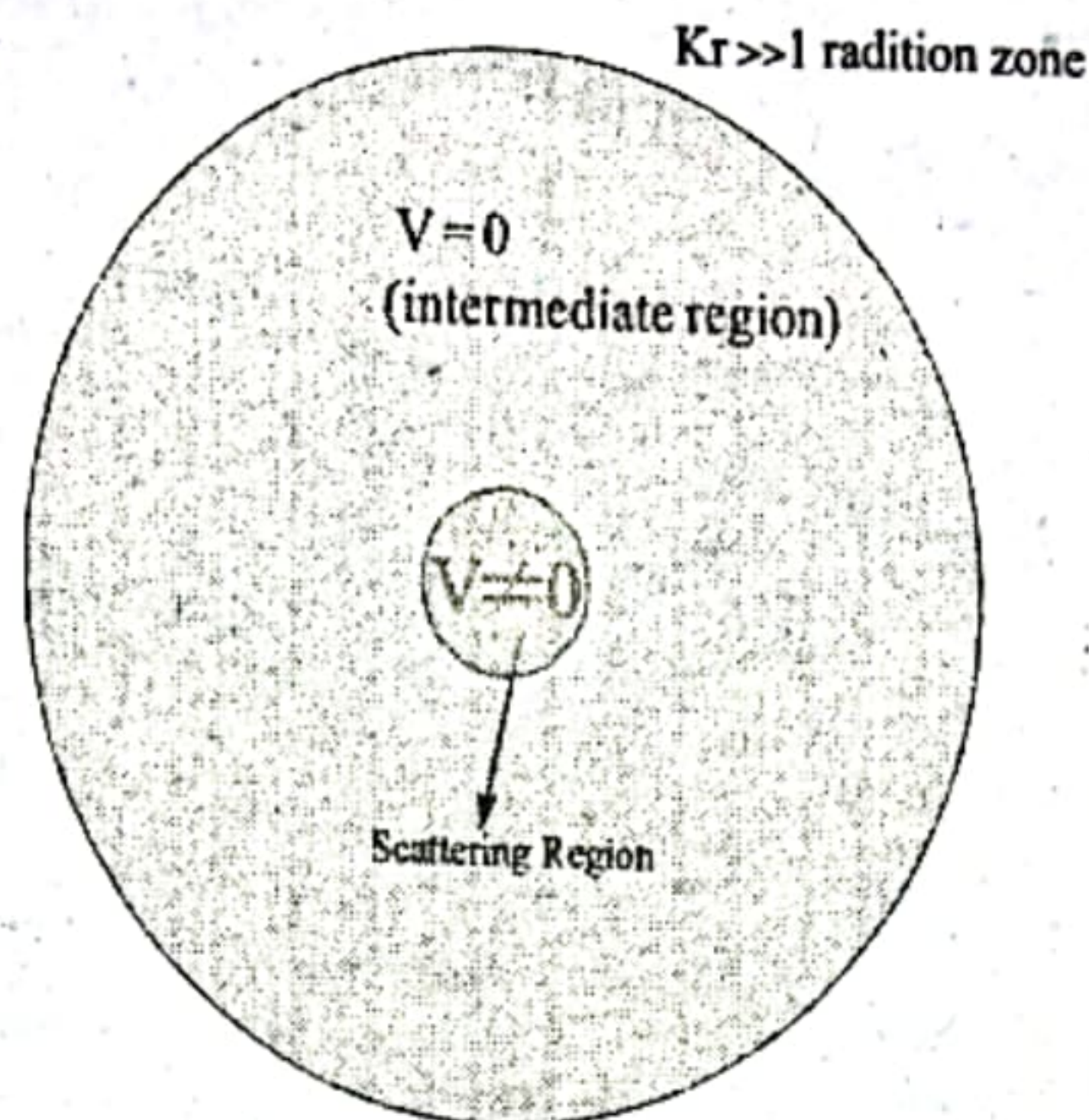


Fig. 4.5. Scattering from a localized potential: the scattering region (darker shading); the intermediate region (lighter shading), and the radiation zone (where $kr \gg 1$)

where, $k^2 = \frac{2mE}{\hbar^2}$. This is the Bessel function equation and general solution is a linear combination of spherical Bessel function.

$$U(r) = A r j_l(kr) + B r n_l(kr)$$

So,

$$R(r) = A j_l(kr) + B n_l(kr)$$

However, neither j_l (sine function) nor n_l (cosine function) represents an outgoing (or incoming) wave. We need a linear combination of j_l and n_l analogous to e^{ikr} (outgoing wave), known as spherical Hankel function

$$h_l'(x) = j_l(x) + i n_l(x)$$

At large r , $h_l'(kr)$ goes like $\frac{e^{ikr}}{r}$ for outgoing waves

$$R(r) = C_l h_l'(kr)$$

Where C_l is a coefficient. Thus the exact wavefunction Eq.(4.11) for $V(r) = 0$ becomes

$$\psi(r, \theta, \phi) = \sum_{l=0}^{\infty} C_l h_l'(kr) Y_l^m(\theta, \phi)$$

As $V(r)$ is spherically symmetric potential, scattered wavefunction must not depend on ϕ , hence $m = 0$ and $Y_l^0(\theta, \phi) = P_l(\cos\theta)$. Also, for very large r

$$h_l'(kr) \sim (-i)^{l+1} \frac{e^{ikr}}{kr}$$

So,

$$\psi(r, \theta) = \sum_{l=0}^{\infty} C_l (-i)^{l+1} \frac{e^{ikr}}{kr} P_l(\cos\theta) \quad (4.16)$$

Each term of this equation is a partial wave. The scattering amplitude is determined by matching Eq.(4.16) to the Eq.(4.5)

$$\psi(r, \theta) = A \left[e^{ikr} + f(\theta) \frac{e^{ikr}}{r} \right] \quad (4.17)$$

The scattering amplitude is

$$f(\theta) = \frac{1}{k} \sum_{l=0}^{\infty} C_l (-i)^{l+1} P_l(\cos\theta) \quad (4.18)$$

and the total cross section is

$$\sigma = \int_{4\pi} |f(\theta)|^2 d\Omega$$

After putting the value of $f(\theta)$ and calculation for $l = l'$

$$\sigma = \frac{1}{k^2} \sum_{l=0}^{\infty} |C_l|^2 \quad (4.19)$$

4.4 The Born Approximation

In Born approximation, $V(r)$ is localized about $r = 0$ (i.e. Potential drops to zero outside some finite region) and the incoming plane wave is changed slightly by the weak potential (i.e. incident and scattering particle or wave are in plane wave states). Moreover, the potential is weak as compared to incident particle and that's why incident and scattering particles have same momentum (i.e. $K = K'$ magnitudes are same but directions are different) (see Fig. (4.6)).

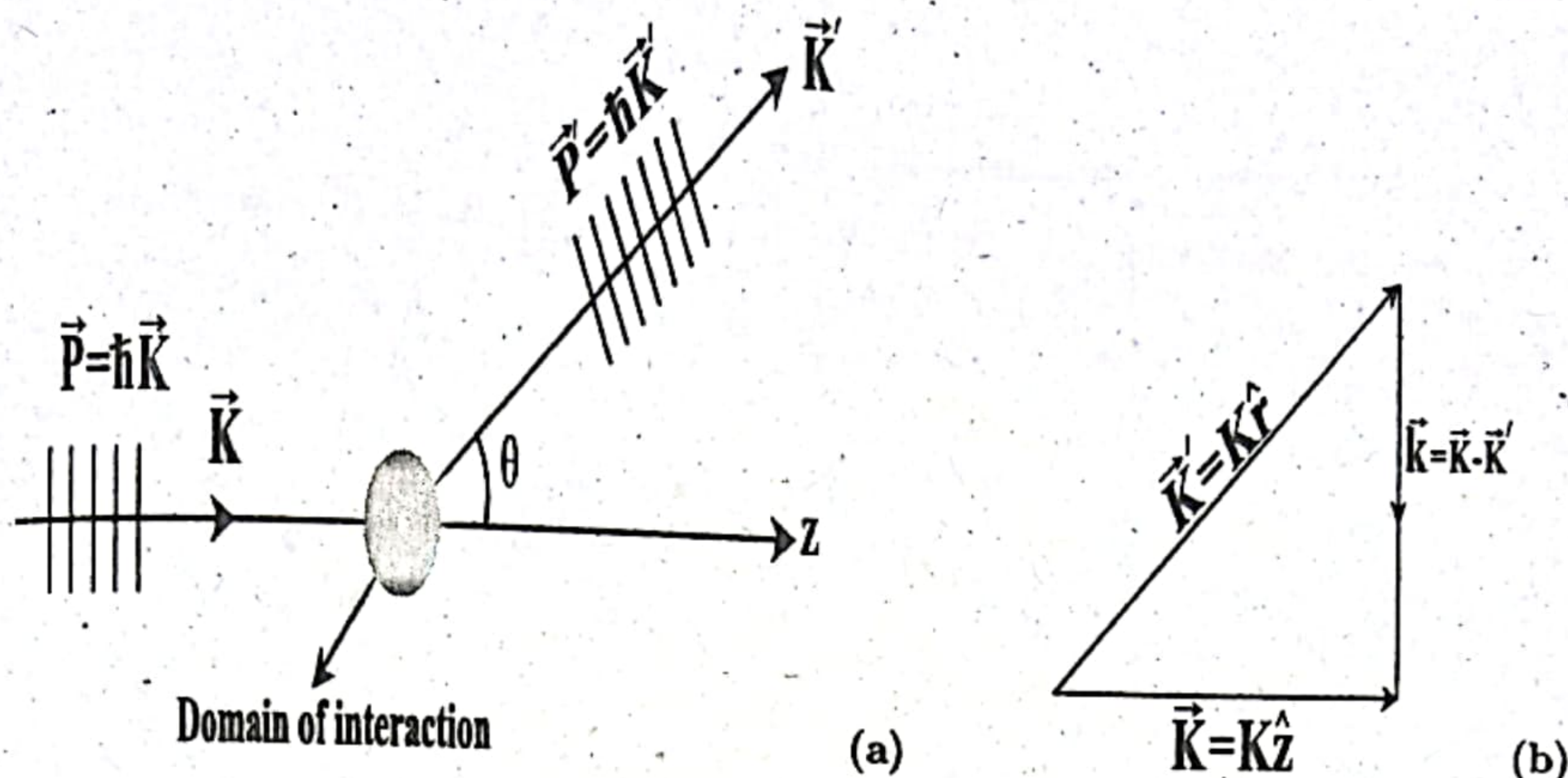


Fig. 4.6. (a) In Born approximation, incident and scattered particles are in plane-wave states (b) Two wave vectors in the Born approximation

In this case, the perturbation Hamiltonian is the interaction potential V which is turned on during the time that the incident particle is in the domain of potential. The incident potential enters the range of interaction with momentum $\hbar K$ and leave the range of interaction with momentum $\hbar K'$.

Let us suppose that the scattering experiment is performed in a large cubical box of volume L^3 . The plane wave states corresponding to K and K' are

$$|K\rangle = \frac{e^{iKr}}{L^{3/2}} \quad (\text{Incident plane wave})$$

$$|K'\rangle = \frac{e^{iK'r}}{L^{3/2}} \quad (\text{Scattered plane wave})$$

According to Fermi Golden rule the rate of transition from K to K' state, caused by the Harmonic perturbing potential $V(r)$

$$\omega_{KK'} = \frac{2\pi}{\hbar} \rho(E_{K'}) \left| \langle K' | V | K \rangle \right|^2 \quad (4.20)$$

Where $\rho(E_{K'})$ is density of final states in all 4π solid angle,

$$\rho(E_{K'}) = \frac{mL^3 K'}{2\pi^2 \hbar^2}$$

As we know that the number of particles scattered into $d\Omega$ per second is $J_{in} d\sigma$

$$dN = J_{in} d\sigma \quad (4.21)$$

$J_{in} = \frac{\hbar K}{mL^3}$ = incident particles per unit area per unit time.

To select those scattered states that lie in the direction $d\Omega$ about K' , we multiply $\omega_{KK'}$ by the ratio $\frac{d\Omega}{4\pi}$.

$$dN = \omega_{KK'} \frac{d\Omega}{4\pi} \quad (4.22)$$

Comparing Eq.(4.21) and Eq.(4.22)

$$\begin{aligned} \omega_{KK'} \frac{d\Omega}{4\pi} &= \frac{\hbar K}{mL^3} d\sigma \\ \frac{d\sigma}{d\Omega} &= \omega_{KK'} \frac{mL^3}{4\pi \hbar K} \end{aligned} \quad (4.23)$$

Using Eq.(4.20) and Eq.(4.23)

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= |f(\theta)|^2 = \frac{mL^3}{4\pi \hbar^2} \frac{2\pi}{\hbar} \frac{mL^3 K'}{2\pi^2 \hbar^2} |\langle K' | V | K \rangle|^2 \\ \frac{d\sigma}{d\Omega} &= |f(\theta)|^2 = \left(\frac{mL^3}{2\pi \hbar^2} \right)^2 \frac{K'}{K} |\langle K' | V | K \rangle|^2 \end{aligned}$$

According to Born's approximation, since particles suffer no loss in energy in the scattering process so $K = K'$

$$|f(\theta)|^2 = \left(\frac{mL^3}{2\pi \hbar^2} \right)^2 \left| \int \frac{e^{-iK'r}}{L^{3/2}} V \frac{e^{iKr}}{L^{3/2}} d^3r \right|^2$$

where $r \cdot K = rK \cos \theta$ and using -ve sign as a convention, we get

$$\begin{aligned} f(\theta) &= -\frac{m}{2\pi \hbar^2} \int e^{ir \cdot (K - K')} V(r) d^3r \\ &= -\frac{m}{2\pi \hbar^2} \int V(r) e^{iKr \cos \theta} r^2 \sin \theta dr d\theta d\phi \\ &= -\frac{m}{2\pi \hbar^2} \int_0^{2\pi} d\phi \int_0^\infty V(r) r^2 \int_0^\pi d\theta \sin \theta e^{iKr \cos \theta} dr \\ &= -\frac{m2\pi}{2\pi \hbar^2} \int_0^\infty V(r) r^2 \frac{2 \sin Kr}{Kr} dr \end{aligned}$$

$$f(\theta) = -\frac{2m}{\hbar^2 K} \int_0^\infty dr V(r) r \sin Kr \quad (4.24)$$

This is the standard form of the Born approximation. We infer that the Born approximation is valid for large incident energies and weak scattering potentials. That is, when the average interaction energy between the incident particle and the scattering potential is much smaller than the particle's incident kinetic energy, the scattered wave can be considered to be a plane wave.

4.5 Frame of References

Scattering experiments are carried out in two frames

1. **Lab Frame:** - A frame in which the target is initially at rest while the particles are moving.
2. **Center of Mass Frame :-** A frame in which the center of mass of the projectiles target system is at rest (before and after collision)

4.6 Review Questions

- 4.1 Why differential area $d\sigma$ and solid angle $d\Omega$ are directly proportional to each other?
- 4.2 What is role of impact parameter b in scattering?
- 4.3 Show that total cross section area σ depends over all solid angles.
- 4.4 Define incident and scattered density.
- 4.5 Define the relation between differential scattering and scattering amplitude.
- 4.6 Differentiate between incident and scattered wavefunction.
- 4.7 Differentiate between spherical Bessel and Hankel functions.
- 4.8 Differentiate between partial wave and Born approximation.
- 4.9 Discuss the validity of Born approximation.
- 4.10 Differentiate between Lab and CM frame.



4.7 Solved Problems

4.1. A beam of particles is incident normally on a thin metal foil of thickness t . if N_0 is the number of nuclei per unit volume of the foil, show that the fraction of incident particles scattered in the direction (θ, ϕ) is $\sigma(\theta, \phi) N_0 t d\Omega$, where $d\Omega$ is the small solid angle in the direction (θ, ϕ) .

Solution

We know that, the differential scattering cross-section is

$$\sigma(\theta, \phi) = \frac{n/d\Omega}{N}$$

Where n is the number scattered into solid angle $d\Omega$ in the direction (θ, ϕ) in unit time and N is the incident flux. Hence,

$$n = \sigma(\theta, \phi) N d\Omega$$

This is the number scattered by a single nucleus. The number of nuclei in a volume $At = N_0 At$. The number scattered by $N_0 At$ nuclei $= \sigma(\theta, \phi) N d\Omega N_0 At$. Thus, Number of particles striking an area $A = NA$. Fraction scattered in the direction

$$\frac{(\theta, \phi) \sigma(\theta, \phi) N d\Omega N_0 At}{NA}$$

$$(\theta, \phi) \sigma(\theta, \phi) N_0 t d\Omega$$



4.2. In the theory of scattering by a fixed potential, the asymptotic form of the wave function is

$$\psi \xrightarrow{r \rightarrow \infty} A \left[e^{ikz} + f(\theta, \phi) \frac{e^{ikr}}{r} \right]$$

Obtain the formula for scattering cross-section in terms of the scattering amplitude $f(\theta, \phi)$.

Solution

The probability current density $j(r, t)$ is given by

$$j(r, t) = \frac{i\hbar}{2\mu} (\psi \nabla \psi^* - \psi^* \nabla \psi)$$

If $j(r, t)$ is calculated with the given wave function, we get interference terms between the incident and scattered wave. In the experimental arrangements, these do not appear. Hence we calculate the incident and scattered probability current densities J_i and J_s separately. The value of J_i due to e^{ikz} is

$$J_i = \frac{i\hbar}{2\mu} [|A|^2 (-ik) - |A|^2 (-ik)]$$

$$J_i = \frac{\hbar k |A|^2}{\mu}$$

The scattered probability current density

$$J_s = \frac{i\hbar}{2\mu} |A|^2 |f(\theta, \phi)|^2 \left[-\frac{ik}{r^2} - \frac{1}{r^3} - \frac{ik}{r^2} + \frac{1}{r^3} \right]$$

$$J_s = \frac{\hbar k}{\mu} |A|^2 |f(\theta, \phi)|^2 \frac{1}{r^2}$$

In the above equation, $\frac{1}{r^2}$ is the solid angle subtended by unit area of the detector at the scattering center. The differential scattering cross-section $\sigma(\theta)$ = probability current density of the scattered wave per unit solid angle / probability current density of the incident wave

$$\sigma(\theta) = \frac{\left(\frac{\hbar k}{\mu}\right) |A|^2 |f(\theta, \phi)|^2}{\frac{\hbar k}{\mu} |A|^2} = |f(\theta, \phi)|^2$$

4.3. Using Born approximation, calculate the differential and total cross-sections for scattering of a particle of mass m by the δ -function potential $V(r) = g\delta(r)$, g -constant.

Solution

From the equation, the scattering amplitude

$$f(\theta) = -\frac{m}{2\pi\hbar^2} \int \exp(iq \cdot r') V(r') d\tau'$$

Where $q = k - k'$ and $|\theta| = 2k \sin \frac{\theta}{2}$. Here, k and k' are respectively, the wave vectors of the incident and scattered waves. Substituting the value of $V(r)$, we get

$$f(\theta) = -\frac{mg}{2\pi\hbar^2} \int \exp(iq \cdot r') \delta(r') d\tau'$$

Using the definition of δ -function, we get

$$f(\theta) = -\frac{mg}{2\pi\hbar^2}$$

The differential scattering cross-section is

$$\sigma(\theta) = |f(\theta)|^2 = \frac{m^2 g^2}{4\pi^2 \hbar^4}$$

Since the distribution is isotropic, the total cross-section is given by

$$\sigma = 4\pi\sigma(\theta) = \frac{m^2 g^2}{\pi \hbar^4}$$



4.4. Write the asymptotic form of the wave function in the case of scattering by a fixed potential and explain. Also, what is Born approximation?

Solution

The general asymptotic solution is

$$\psi \xrightarrow{r \rightarrow \infty} A \left[e^{ikz} + f(\theta, \phi) \frac{e^{ikr}}{r} \right]$$

Where A is a constant. In this, the part e^{ikz} represents the incident plane wave along the z -axis. The wave vector k is given by

$$k^2 = \frac{2mE}{\hbar^2},$$

Where E is the energy. The second term of equation (1) represents the spherically diverging scattered wave. The amplitude factor $f(\theta, \phi)$ is called the scattering amplitude.

A general analysis of the scattering problem requires expressing the wave function in the form of an integral equation. In this expression for the wave function, the wave function appears under the integral sign. In the first Born approximation, $\psi(r)$ in the integrand is replaced by the incoming plane wave $e^{ik \cdot r}$. This leads to an improved value for the wave function which is used in the integral in the second Born approximation. This iterative procedure is continued till the input and output ψ 's are almost equal.



4.5. What is the formula for the first Born approximation for scattering amplitude $f(\theta)$? Under what condition is the Born approximation valid?

Solution

In the first Born approximation, the scattering amplitude

$$f(\theta) = -\frac{2\mu}{\hbar^2} \int_0^\infty \frac{\sin(qr')}{qr'} V(r') r'^2 dr'$$

Where $q\hbar$ is the momentum transfer from the incident particle to the scattering potential and

$$|q| = 2k \sin \frac{\theta}{2}$$

With angle θ being the scattering angle, $V(r)$ the potential, and μ the reduced mass. Moreover, the Born approximation is valid for weak potentials at high energies.



4.8 Multiple Choice Questions

- The distance between incident and target nucleus is
a) Impact parameter b) Impact scattering c) impact element d) None of these
- What kind of wave we get when plane wave strikes with target
a) Plane wave b) Spherical wave c) Light wave d) Wave packet
- In quantum scattering, we take incident particle in the form of
a) Solid particle b) Solid field c) Field form d) Liquid form
- In quantum scattering, motion of incident particle is in
a) One dimension b) Two dimension c) Three dimension d) Zero dimension
- $d\sigma$ is directly proportional to
a) $d\Omega$ b) dV c) $D(\theta)$ d) dA
- If $kr \gg 1$, the region will be called as
a) Radiation Zone b) Intermediate region c) Scattering region d) Closed region
- $V(r)$ can be spherically — — — — — potential
a) Symmetric b) Anti-symmetric c) Non-zero d) All
- For large values of r , potential $V(r)$ approaches to
a) 0 b) 1 c) ∞ d) None
- Born approximation is valid for incident particle with
a) Large energy b) Small energy c) Strong potential d) None
- In the scattering of Born approximation, particles have
a) Loss of energy b) Energy Conserved c) $k \neq k$ d) None of these

Answers

1	a	2	b	3	c	4	a	5	a
6	a	7	a	8	c	9	a	10	c

Chapter 5

Relativistic Quantum Mechanics

"The part of quantum mechanics based on the Schrödinger wave equation which describes the motion of a particle that has a speed approaching the speed of light" is known as Relativistic Quantum Mechanics. "The part of quantum mechanics based on the Schrödinger wave equation describes the particles moving with very low velocities comparing with velocity of light" is known as Non-relativistic Quantum Mechanics. Moreover, old Schrödinger wave theory fails to explain the spin of a particle.

In this chapter we formulate a theory which can describe the motion of a particle, that has a speed approaching to speed of light. The relativistic quantum mechanics is guided by the following points.

1. The theory should be formulated in terms of amplitude function (probability density) as in case of Schrödinger wave function.
2. The description of physical phenomena in this theory should be based upon equation of motion describing the development of system in time.
3. The super position principle should hold and therefore this equation of motion must be linear in the amplitude function.
4. The equation of motion must be invariant under Lorentz transformation.
5. The theory should be consistent with the correspondence principle (i.e. on large level Quantum Mechanics becomes Classical Mechanics).

Special theory of relativity is based on two postulates

- 1 Laws of physics are same for all inertial system.
- 2 Speed of light (c) is valid in all observers and independent of motion of source.

The Schrödinger wave equation for a free particle ($V = 0$) in non-relativistic case in the coordinates representation is given by

$$\begin{aligned}\hat{H} \Psi &= E \Psi \\ \left[\frac{-\hbar^2}{2m} \nabla^2 + V \right] \Psi &= i\hbar \frac{\partial}{\partial t} \Psi \\ \frac{-\hbar^2}{2m} \nabla^2 \Psi &= i\hbar \frac{\partial}{\partial t} \Psi \\ \boxed{i\hbar \frac{\partial}{\partial t} \Psi = \frac{-\hbar^2}{2m} \nabla^2 \Psi} & \quad (5.1)\end{aligned}$$

The different orders of the time and the space derivatives shows that Eq.(5.1) is not Lorentz covariant (an equation that changes its structure under a transition from one inertial system to another).

Special theory of relativity says that equation must be Lorentz invariant. Work on relativistic quantum mechanics was formulated by Schrödinger, Klein and Gordon. They suggested Klein-Gordon equation in 1927 which was a 2nd order wave equation rather than Schrödinger equation. In 1928, the Dirac gave another equation that was related to fermions. The Dirac equation, like the Klein-Gordon equation, possesses the solutions with negative energy which cannot be explained by wave mechanics.

Dirac postulated that the states of negative energy should all be occupied which contain particles with opposite charge (anti-particle). This necessarily leads to a many particle theory or to a quantum field theory. The Schrödinger equation as well as the other rules of old quantum theory remain unchanged. Only the Hamiltonian is changed and now represents a quantized field.

5.1 Klein-Gordon Equation

In order to derive the relativistic wave equation, Klein-Gordon developed an equation for the particles moving with a speed approaching to the speed of light. This equation is called Klein-Gordon equation.

According to the special theory of relatively, energy E , and momentum P , are related by the following relation.

$$E^2 = P^2 c^2 + m_0^2 c^4, \quad (5.2)$$

where m_0 is the rest mass. Replacing E and P by their corresponding quantum mechanical operators and then operating on the wave function, representing the particle, we obtain.

$$\begin{aligned} & \left[i\hbar \frac{\partial}{\partial t} \right]^2 \Psi(r, t) = (-i\hbar \nabla)^2 c^2 + m_0^2 c^4 \Psi(r, t) \\ & i^2 \hbar^2 \frac{\partial^2}{\partial t^2} \Psi(r, t) = [+i^2 \hbar^2 \nabla^2 c^2 + m_0^2 c^4] \Psi(r, t) \\ & -\hbar^2 \frac{\partial^2}{\partial t^2} \Psi(r, t) = -\hbar^2 \nabla^2 c^2 + m_0^2 c^4 \Psi(r, t) \end{aligned}$$

Dividing $\hbar^2$ on both side,

$$\begin{aligned} & -\frac{\partial^2}{\partial t^2} \Psi(r, t) = -\nabla^2 c^2 \Psi(r, t) + \frac{m_0^2 c^4}{\hbar^2} \Psi(r, t) \\ & -\frac{\partial^2}{\partial t^2} \Psi(r, t) c^2 = \left[-\nabla^2 \Psi(r, t) + \frac{m_0^2 c^2}{\hbar^2} \Psi(r, t) \right] \\ & -\frac{1}{c^2} \frac{\partial^2}{\partial t^2} \Psi(r, t) = -\nabla^2 \Psi(r, t) + \frac{m_0^2 c^2}{\hbar^2} \Psi(r, t) \\ & \nabla^2 \Psi(r, t) - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \Psi(r, t) = \frac{m_0^2 c^2}{\hbar^2} \Psi(r, t) \\ & \left[\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right] \Psi(r, t) = \frac{m_0^2 c^2}{\hbar^2} \Psi(r, t) \quad (5.3) \end{aligned}$$

This equation is clearly lorentz covariant. The Eq.(5.3) for $\Psi(r, t)$ is called the free Klein-Gordon equation for the wave function $\Psi(r, t)$ because it does not containing potential ($V=0$). The Klein-Gordon equation is a 2nd order in time variable t , where as the non relativistic Schrodinger wave equation is a first order in time parameter.

5.2 Free Particle Solution of K-G Equation

The free Klein-Gordon equation is

$$\nabla^2 \Psi(r, t) - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \Psi(r, t) = \frac{m_0^2 c^2}{\hbar^2} \Psi(r, t) \quad (5.4)$$

The free particle solution of this equation can be written as

$$\Psi(r, t) = A e^{i(\vec{k} \cdot \vec{r} - \omega t)} \quad (5.5)$$

Differentiate Eq.(5.5) w.r.t. t ,

$$\frac{\partial \Psi}{\partial t} = A(-i\omega) e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

Again differentiating,

$$\frac{\partial^2 \Psi}{\partial t^2} = A(-i\omega)^2 e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

$$\frac{\partial^2 \Psi}{\partial t^2} = A i^2 \omega^2 e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

$$\frac{\partial^2 \Psi}{\partial t^2} = -A \omega^2 e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

$$\frac{\partial^2 \Psi}{\partial t^2} = -A \omega^2 e^{i(\vec{k} \cdot \vec{r} - \omega t)} \quad (5.6)$$

Differentiating Eq.(5.5) w.r.t. r

$$\frac{\partial \Psi}{\partial r} = i k A e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

Differentiating again w.r.t. r ,

$$\frac{\partial^2 \Psi}{\partial r^2} = A(i k)^2 e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

$$\frac{\partial^2 \Psi}{\partial r^2} = A i^2 k^2 e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

$$\frac{\partial^2 \Psi}{\partial r^2} = -A k^2 e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

Or, as $\frac{\partial^2 \Psi}{\partial r^2} = \nabla^2 \Psi$

$$\nabla^2 \Psi = -A k^2 e^{i(\vec{k} \cdot \vec{r} - \omega t)} \quad (5.7)$$

Substituting Eq.(5.5), Eq.(5.6) and Eq.(5.7) in Eq.(5.4)

$$-A k^2 e^{i(\vec{k} \cdot \vec{r} - \omega t)} - A \frac{1}{c^2} - \omega^2 e^{i(\vec{k} \cdot \vec{r} - \omega t)} = \frac{m_o^2 c^2}{\hbar^2} A e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

$$\left(-k^2 + \frac{\omega^2}{c^2} \right) e^{i(\vec{k} \cdot \vec{r} - \omega t)} = \frac{m_o^2 c^2}{\hbar^2} e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

$$\begin{aligned}
 -k^2 + \frac{\omega^2}{c^2} &= \frac{m_o^2 c^2}{\hbar^2} \\
 -\left(k^2 - \frac{\omega^2}{c^2}\right) &= \frac{m_o^2 c^2}{\hbar^2} \\
 \frac{k^2 c^2 - \omega^2}{c^2} &= -\frac{m_o^2 c^2}{\hbar^2} \\
 k^2 c^2 - \omega^2 &= -\frac{m_o^2 c^4}{\hbar^2} \\
 \hbar^2 (k^2 c^2 - \omega^2) &= -m_o^2 c^4 \\
 \hbar^2 k^2 c^2 - \hbar^2 \omega^2 &= -m_o^2 c^4
 \end{aligned} \tag{5.8}$$

We know that, $E = \hbar\omega$; $E^2 = \hbar^2\omega^2$ and $k\hbar = p$; $k^2\hbar^2 = p^2$ Putting the values in Eq.(5.8), we get.

$$\begin{aligned}
 p^2 c^2 - E^2 &= -m_o^2 c^4 \\
 p^2 c^2 + m_o^2 c^4 &= E^2 \\
 E^2 &= c^2 (p^2 + m_o^2 c^2) \\
 E &= \pm c\sqrt{(p^2 + m_o^2 c^2)} \\
 E &= \pm E_p \\
 \therefore E_p &= c\sqrt{(p^2 + m_o^2 c^2)}
 \end{aligned} \tag{5.9}$$

Putting the value of $k = p/\hbar$ and $\omega = E/\hbar$ in Eq.(5.5)

$$\begin{aligned}
 \Psi(r, t) &= Ae^{i(\vec{k} \cdot \vec{r} - \omega t)} \\
 \Psi(r, t) &= Ae^{i\left(\frac{\vec{p}}{\hbar} \cdot \vec{r} - \frac{E}{\hbar} t\right)} \\
 \Psi(r, t) &= Ae^{\frac{i}{\hbar}(\vec{P} \cdot \vec{r} - Et)}
 \end{aligned}$$

As energy is having two values $E = \pm E_p$, thus there are two possible free solutions in the form of plane wave

$$\begin{aligned}
 \Psi_+ &= A_+ e^{\frac{i}{\hbar}(\vec{P} \cdot \vec{r} - E_p t)} \\
 \Psi_- &= A_- e^{\frac{i}{\hbar}(\vec{P} \cdot \vec{r} + E_p t)}
 \end{aligned}$$

The $\pm$ sign corresponds to the fact that +ve and -ve energies occurs here and energy is not bound from below. This means that as a result, the energy spectrum has no ground

state. This large amount of energy was unexpected from the system. Moreover, this scalar theory does not contain spin and only describe particles with zero spin e.g. π mesons (Boson), because here Ψ has a single value.

If the external perturbation allows transition between +ve and -ve energy states. So, for a free particle initially at rest, if particle jumps over the energy states gap between the +ve and -ve energy continue due to external perturbation as shown in Fig. (5.1). We know that,

$$\Delta E = E - (-E) = 2E$$

But for rest mass energy in relativistic effect, it is $\Delta E = 2mc^2$. So, due to this difficulty, K.G. Eq. was rejected.

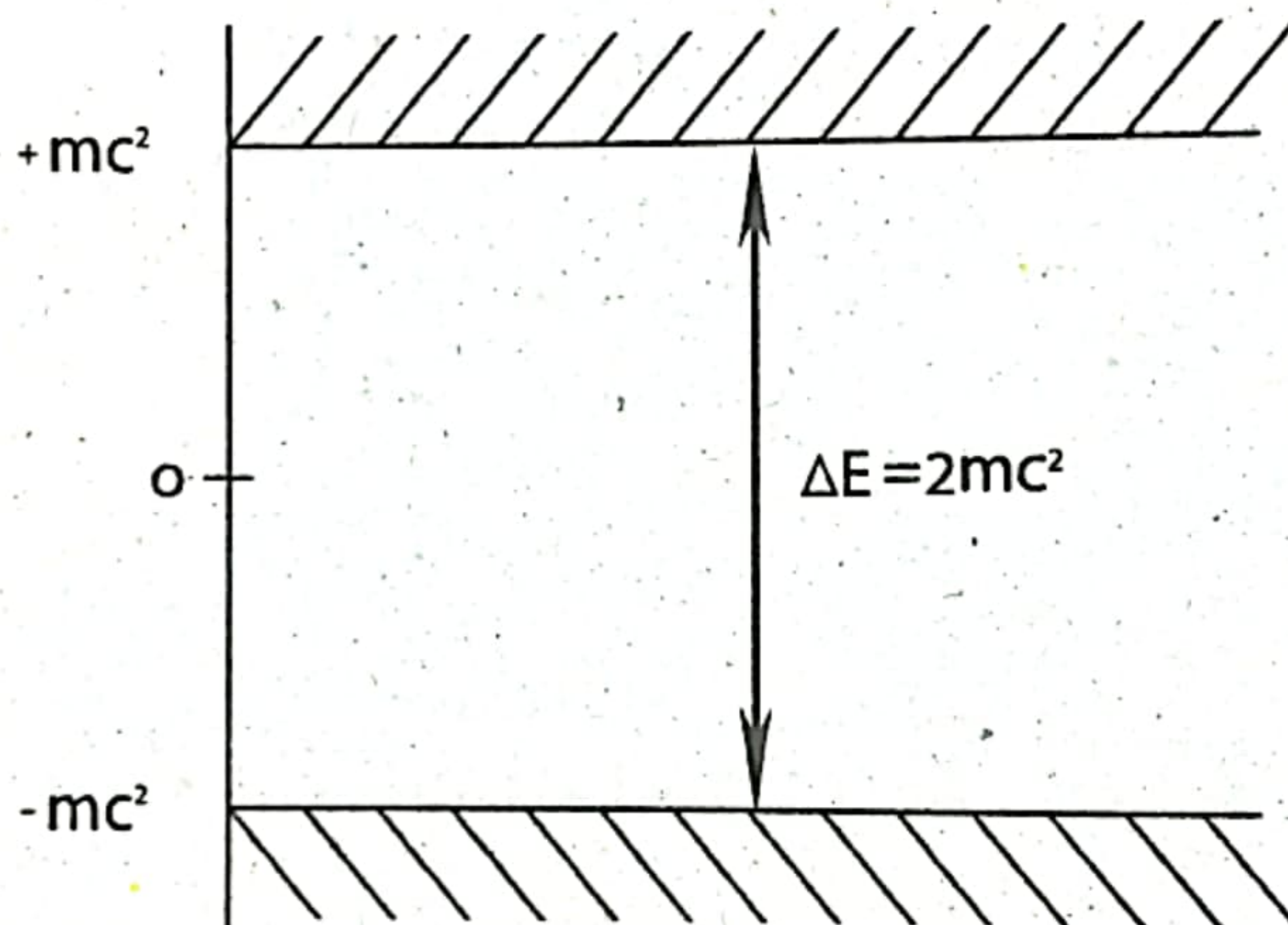


Fig. 5.1. The energy levels of a free particle in K.G. Equation.

In 1934, W. Pauli and V. Weiskoof reinterpreted the K.G. equation as field equation and quantized it by using the formulism of Quantum Field Theory. The K.G. Eq. then becomes a relativistic wave equation for spin-less particles. In this frame work of many particle theory in which -ve energy states are interpreted in terms of anti-particles. It should be noted that number of particles is not conserved because of possibilities of creation and annihilation of particle and anti-particle pairs, but energy remain conserved.

5.3 Equation of Continuity

The non-relativistic probability density is given by

$$\rho(r, t) = |\Psi|^2 = \Psi^* \Psi \quad (5.10)$$

The non relativistic current density $J(r, t)$ is.

$$J(r, t) = \frac{\hbar}{2im_0} (\Psi^* \nabla \Psi - \Psi \nabla \Psi^*) \quad (5.11)$$

The corresponding non-relativistic equation of continuity is.

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \vec{J} = 0$$

Equation of continuity describes the transport of some conserved quantities. To obtain the equation of continuity in relativistic case, we use the Klein-Gordon equation;

$$\left[\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right] \Psi = \frac{m_0^2 c^2}{\hbar^2} \Psi \quad (5.12)$$

Taking complex conjugate of Eq.(5.12)

$$\left[\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right] \Psi^* = \frac{m_0^2 c^2}{\hbar^2} \Psi^* \quad (5.13)$$

Multiplying Eq.(5.12) by Ψ^* , from the left and multiplying equation Eq.(5.13) by Ψ , from the left and then subtracting equation Eq.(5.13) from Eq.(5.12),

$$\begin{aligned} \Psi^* \left(\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) \Psi - \Psi \left(\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) \Psi^* &= \frac{m_0^2 c^2}{\hbar^2} |\Psi|^2 - \frac{m_0^2 c^2}{\hbar^2} |\Psi|^2 \\ \Psi^* \nabla^2 \Psi - \Psi^* \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \Psi - \Psi \nabla^2 \Psi^* + \Psi \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \Psi^* &= 0 \\ \Psi^* \nabla^2 \Psi - \Psi \nabla^2 \Psi^* - \Psi^* \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \Psi + \Psi \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \Psi^* &= 0 \\ \Psi^* \nabla^2 \Psi - \Psi \nabla^2 \Psi^* - \frac{1}{c^2} \left[\Psi^* \frac{\partial^2}{\partial t^2} \Psi - \Psi \frac{\partial^2}{\partial t^2} \Psi^* \right] &= 0 \end{aligned}$$

Applying the vector identity on the first two terms in the above equation i.e. $\nabla^2 = \vec{\nabla} \cdot \vec{\nabla}$

$$\begin{aligned}\psi^* \vec{\nabla} \cdot \vec{\nabla} \psi - \psi \vec{\nabla} \cdot \vec{\nabla} \psi^* - \frac{1}{c^2} \left[\psi^* \frac{\partial^2}{\partial t^2} \psi - \psi \frac{\partial^2}{\partial t^2} \psi^* \right] &= 0 \\ \vec{\nabla} \cdot (\psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^*) - \frac{1}{c^2} \frac{\partial}{\partial t} \left[\psi^* \frac{\partial}{\partial t} \psi - \psi \frac{\partial}{\partial t} \psi^* \right] &= 0\end{aligned}$$

Multiplying throughout by $\frac{\hbar}{2im_0}$, we get,

$$\begin{aligned}\frac{\hbar}{2im_0} \vec{\nabla} \cdot (\psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^*) - \frac{\hbar}{c^2 2im_0} \frac{\partial}{\partial t} \left[\psi^* \frac{\partial}{\partial t} \psi - \psi \frac{\partial}{\partial t} \psi^* \right] &= 0 \\ \frac{\hbar}{2im_0} \vec{\nabla} \cdot (\psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^*) - \frac{\hbar}{c^2 2im_0} \frac{\partial}{\partial t} \left[\psi^* \frac{\partial}{\partial t} \psi - \psi \frac{\partial}{\partial t} \psi^* \right] &= 0\end{aligned}$$

As $1/i = -i$,

$$\frac{\hbar}{2im_0} \vec{\nabla} \cdot (\psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^*) + \frac{i\hbar}{c^2 2m_0} \frac{\partial}{\partial t} \left[\psi^* \frac{\partial}{\partial t} \psi - \psi \frac{\partial}{\partial t} \psi^* \right] = 0$$

Rearranging we have,

$$\begin{aligned}\frac{\partial}{\partial t} \frac{i\hbar}{c^2 2m_0} \left[\psi^* \frac{\partial}{\partial t} \psi - \psi \frac{\partial}{\partial t} \psi^* \right] + \vec{\nabla} \cdot \frac{\hbar}{2im_0} (\psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^*) &= 0 \\ \frac{\partial}{\partial t} \rho_r + \vec{\nabla} \cdot \vec{J}_r &= 0\end{aligned}$$

Where, relativistic probability density

$$\rho_r = \frac{i\hbar}{2m_0 c^2} \left[\psi^* \frac{\partial}{\partial t} \psi - \psi \frac{\partial}{\partial t} \psi^* \right] \quad (5.14)$$

Relativistic current density

$$J_r = \frac{\hbar}{2im_0} (\psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^*) \quad (5.15)$$

On comparison of the results of relativistic approach with that of non-relativistic approach, we see that Eq.(5.11) and Eq.(5.15) are the same; but equation Eq.(5.10) and equation Eq.(5.14) are not same.

5.4 Limitations of Klein-Gordon Equation

1st Difficulty

The probability density for a particle is not possible. We know that Eq.(5.14) becomes.

$$\rho_r = \frac{i\hbar}{2m_0c^2} \left[\Psi^* \frac{\partial}{\partial t} \Psi - \Psi \frac{\partial}{\partial t} \Psi^* \right] \quad (5.16)$$

As ρ_r denotes the probability and it must be non-negative i.e. positive. This is the fundamental difficulty of accepting Klein-Gordon equation as a relativistic equation in quantum mechanics.

2nd Difficulty

Another problem with K.G equation is that it does not represent a particle with spin $\frac{1}{2}$ (fermions). This is because, Klein-Gordon equation i.e.

$$\left(\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) \Psi_{(r,t)} = \frac{m_0^2 c^2}{\hbar^2} \Psi_{(r,t)}$$

is an equation for one component only, the single component is Ψ itself. For a spin S , there are $(2S + 1)$ values, For $S = 0$; $(m - s = 2S + 1) = \{2(0) + 1\} = 1$ value. Thus K.G equation is for a particle $S = 0$. So this equation does not represent a particle whose spin is $\frac{1}{2}$. Thus it can be used to describe particles of zero spin such as pion and kaon.

These difficulties were removed by Dirac 1st order differential equation.

5.5 Dirac Equation

In 1928, P.A.M Dirac discovered the relativistic wave equation with a definite positive probability density. Dirac equation explains the particles of spin $1/2$ e.g electron. In non relativistic quantum theory, particles of spin $1/2$ are described by the two spin states

$$\left(S_z = m_s \hbar \quad ; \quad m_s = \pm \frac{1}{2} \right)$$

In relativistic theory, it is also considering the fact of anti-particle having the same mass and spin but of opposite charge, we need, a four component wave function. This was the

achievement of Dirac equation that enable to predict the existence of positron. By analogy with non-relativistic quantum mechanics, Dirac started his equation by a wave equation of the form.

$$i\hbar \frac{\partial \Psi}{\partial t}(r, t) = H\Psi(r, t) \quad (5.17)$$

This Schrödinger equation is linear in $\frac{\partial}{\partial t}$ and not quadratic like K.G eq. In relativistic theory, the spatial coordinates (x, y, z) of space-time must have the same order as the time coordinate, so H is expected to be linear (1st order) in space derivatives $\frac{\partial}{\partial x_k}$ ($k = 1, 2, 3$) and hence density will be positive. The wavefunction $\Psi(r, t)$ in Eq.(5.17) is assumed to have N -components $\Psi_i(r, t)$ $i = 1, 2 \dots N$ and hence Ψ may be written as a column vector.

$$\Psi = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_N \end{pmatrix}$$

As in case of free particle, H is independent of r and t , the Dirac Hamiltonian H is linear in momentum and the rest energy $m_0 c^2$, may be written as.

$$H = c\alpha \cdot \hat{P} + \beta m_0 c^2 \quad (5.18)$$

α and β are dimensionless. As $\hat{P} = -i\hbar \hat{\nabla}$ has three components so α also has three components.

$$H = c \sum_{k=1}^3 \alpha_k \hat{P}_k + \beta m_0 c^2$$

Put Eq.(5.18) in Eq.(5.17) and remembering $E = i\hbar \frac{\partial}{\partial t}$, Dirac equation for free particle is

$$(c\alpha \cdot \hat{P} + \beta m_0 c^2) \Psi = E\Psi$$

$$(E - c\alpha \cdot \hat{P} - \beta m_0 c^2) \Psi = 0 \quad (5.19)$$

In order to determine α_k ($k = 1, 2, 3$) and β , we first require that solution of free particle Dirac Eq.(5.19) must also be a solution of free particle Klein-Gordon equation

$$(E^2 - \hat{P}^2 c^2 - m_o^2 c^4) \Psi = 0 \quad (5.20)$$

For making same order, we multiply Eq.(5.19) on the left by the operator $(E + c\bar{\alpha}.\hat{P} + \beta m_o c^2)$, we obtain 2nd order equation.

$$(E + c\alpha.\hat{P} + \beta m_o c^2) (E - c\bar{\alpha}.\hat{P} - \beta m_o c^2) \Psi = 0$$

$$\left(E^2 - (c\alpha.\hat{P} + \beta m_o c^2)^2 \right) \Psi = 0$$

$$\therefore (a + b)^2 = a^2 + b^2 + ab + ba$$

After calculations.

$$\left[E^2 - c^2 \left(\sum_{k=1}^3 (\alpha_k)^2 (P_k)^2 + \sum_{k < l=0}^N (\alpha_k \alpha_l + \alpha_l \alpha_k) P_k P_l \right) - m_o^2 c^4 \beta^2 \right] \Psi = 0 \quad (5.21)$$

This Dirac equation Eq.(5.21) and Klein-Gordon equation Eq.(5.20) will be same, when

$$\alpha_1^2 = \alpha_2^2 = \alpha_3^2 = \beta^2 = 1$$

$$\{\alpha_1, \alpha_2\} (= \alpha_1 \alpha_2 + \alpha_2 \alpha_1) = 0$$

$$\{\alpha_2, \alpha_3\} = \{\alpha_3, \alpha_1\} = 0$$

$$\{\alpha_1, \beta\} = \{\alpha_2, \beta\} = \{\alpha_3, \beta\} = 0$$

As α_k and β do not commute, they cannot be numbers. So they are matrices of even rank because Eigen values of α_k and β are ± 1 . This anti commuting properties are obeyed by pauli spin matrices (α_k), so

$$\alpha_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix}_{4 \times 4} \quad (\because k = 1, 2, 3)$$

$$\beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}_{4 \times 4}$$

This is Dirac standard representation.

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_{2 \times 2}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}_{2 \times 2}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_{2 \times 2}$$

This means that wavefunction is also having four components.

$$\Psi = \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix}$$

Dirac equation not only describe the spin but also contains the -ve energy states.

5.6 Hole Theory

Dirac equation gives four independent solutions. Two for +ve energy and two for -ve energy states. The -ve energy states can not be ignored on the basis that they are unphysical. Since, all the four solutions together form a complete set, i.e. $\sum_{i=1}^4 \Psi_i \Psi_i^* = I$. This reflects that, electron in the +ve energy states can make transition to -ve energy states at the estimated rate of 10^{-8} sec. This is disastrous and no stable atom is possible if such transitions are allowed to -ve energy states. Dirac gives a bold suggestion in the form of *Hole Theory*, to overcome this difficulty. According to this theory -ve energy states are filled by electrons. The Dirac vacuum is one in which all -ve energy states are filled and all +ve energy states are empty. Thus, Pauli exclusion principle does not allow any electron in the +ve energy states to make transition to -ve energy states which are all occupied. -ve energy electrons can absorb radiation and jump into +ve energy states. Thus Dirac

equation together with hole theory predicts the existence of positron. In 1932, Anderson discovered the positron experimentally and got Nobel prize in 1936.

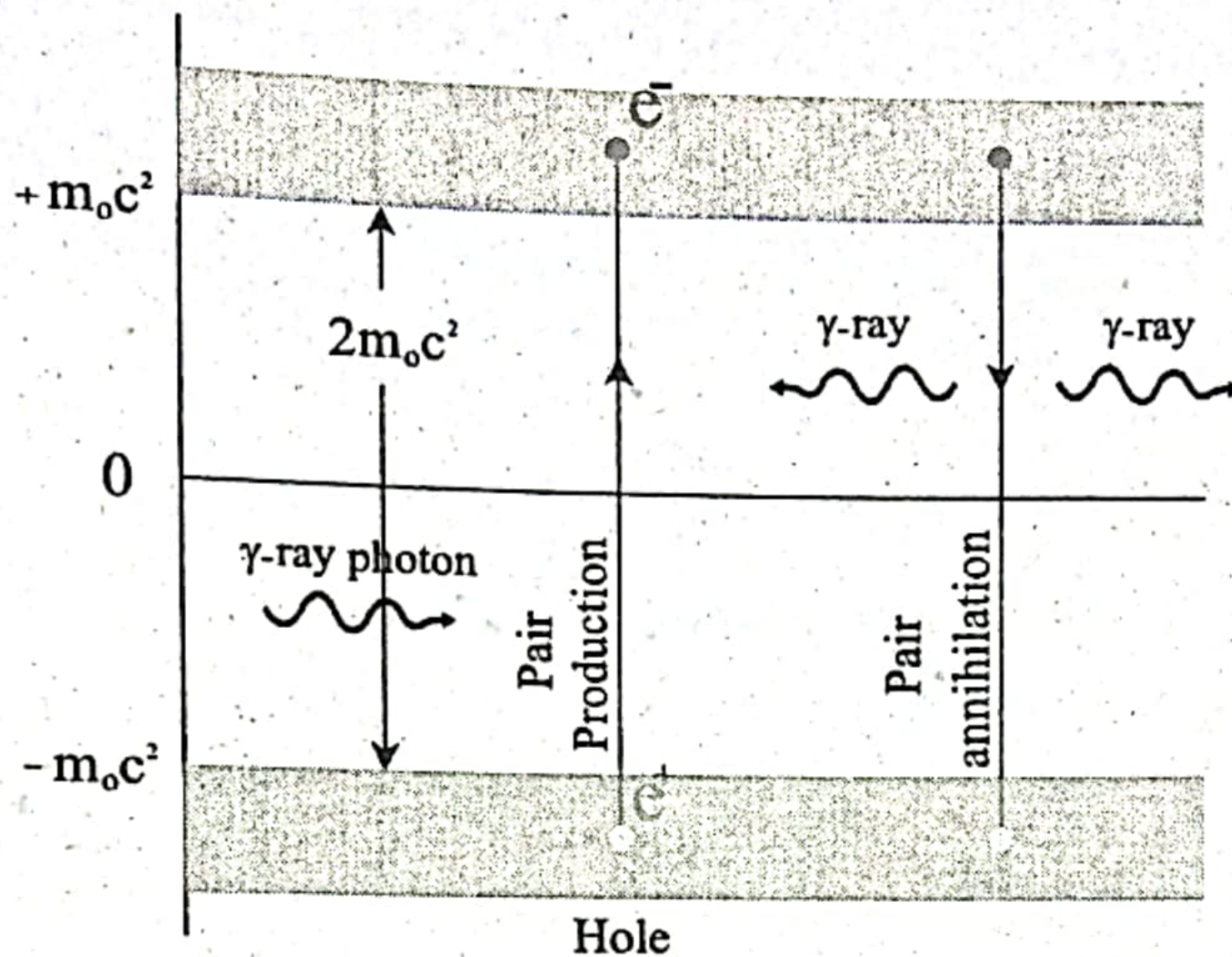


Fig. 5.2. The energy levels of a free Dirac particle.

Positron has many application such as large beam life time positron emission tomography (PET), positron in synchrotron light source, positronium annihilation life time spectroscopy.

5.7 Review Questions

- 5.1 Differentiate between relativistic and non-relativistic quantum mechanics.
- 5.2 Why K.G. Eq. describe the particles with zero spin?
- 5.3 Define two difficulties of K. G. Eq.
- 5.4 Differentiate between K. G. Eq. and Dirac Eq.
- 5.5 Define Lorentz invariant transformation.
- 5.6 Write down the Dirac spinors.
- 5.7 Define Pauli spin matrices.
- 5.8 Why Dirac Eq. explain particles with spin $\frac{1}{2}$ particles?
- 5.9 Explain negative energy states.
- 5.10 What are the potential applications of positron.



5.8 Solved Problems

5.1. Write Dirac's equation for a free particle. Find the probability density and the probability current density in Dirac's formalism.

Solution

Dirac's equation for a free particle is

$$i\hbar \frac{\partial}{\partial t} \Psi(r, t) - i\hbar \alpha \cdot \nabla \Psi + \beta mc^2 \Psi \quad (5.22)$$

Here, α and β are 4×4 matrices and $\Psi(r, t)$ is a four-column vector. The Hermitian conjugate of above equation is

$$i\hbar \frac{\partial}{\partial t} \Psi^*(r, t) - i\hbar \alpha \cdot \nabla \Psi^* + \beta mc^2 \Psi^* \quad (5.23)$$

Multiplying Eq(5.22) by $\Psi^\dagger$ on left, Eq(5.23) by Ψ on right, and subtracting one from the other, we get

$$i\hbar \left(\Psi^\dagger \frac{\partial \Psi}{\partial t} - \frac{\partial \Psi^\dagger}{\partial t} \Psi \right) = -i\hbar (\Psi^\dagger \alpha \cdot \nabla \Psi + \nabla \Psi^\dagger \cdot \alpha \Psi)$$

$$\begin{aligned}\frac{\partial}{\partial t} (\Psi^\dagger \Psi) + \nabla \cdot (c \Psi^\dagger \alpha \Psi) &= 0 \\ \frac{\partial}{\partial t} P(r, t) + \nabla \cdot j(r, t) &= 0\end{aligned}\quad (5.24)$$

Where,

$$j(r, t) = c \Psi^\dagger \alpha \Psi \quad ; \quad P(r, t) = \Psi^\dagger \Psi$$

Eq(5.24) is the continuity equation and the equation $P(r, t)$ and $j(r, t)$ are the probability density and probability current density, respectively.



5.2. For a Dirac particle moving in a central potential, show that the orbital angular momentum is not a constant of motion.

Solution

In the Heisenberg picture, the time rate of change of the $L = r \times p$ is given by

$$i\hbar \frac{dL}{dt} [L, H]$$

Its x-component is

$$i\hbar \frac{d}{dt} L_x [L_x, H] = [yp_z - zp_y, c\alpha \cdot p + \beta mc^2]$$

Since α and β commute with r and p ,

$$\begin{aligned}i\hbar \frac{d}{dt} L_x &= [yp_z, c\alpha_y p_y] - [zp_y, c\alpha_z p_z] \\ i\hbar \frac{d}{dt} L_x &= c[y, p_y] p_z \alpha_y - c[z, p_z] p_y \alpha_z \\ &= ci\hbar p_z \alpha_y - ci\hbar p_y \alpha_z \\ &= ci\hbar (p_z \alpha_y - p_y \alpha_z)\end{aligned}$$

Which shows that L_x is not a constant of motion. Similar relations hold good for L_y and L_z components. Hence the orbital angular momentum L is not a constant of motion.



5.3. If one wants to write the relativistic energy E of a free particle as

$$\frac{E^2}{c^2} (= \alpha \cdot p + \beta mc)^2,$$

Show that α 's and β 's have to be matrices and establish that they are non-singular and Hermitian.

Solution

The relativistic energy (E) of a free particle is given by

$$E^2 = c^2 p^2 + m^2 c^4 = c^2 (p^2 + m^2 c^2)$$

When E^2/c^2 is written as given in the problem,

$$\begin{aligned} p^2 + m^2 c^2 & (= \alpha \cdot p + \beta mc)^2 \\ &= \alpha_x^2 p_x^2 + \alpha_y^2 p_y^2 + \alpha_z^2 p_z^2 \\ &+ \beta^2 m^2 c^2 (+\alpha_x \alpha_y + \alpha_y \alpha_x) p_x p_y (+\alpha_x \alpha_z + \alpha_z \alpha_x) p_x p_z \\ &(+\alpha_y \alpha_z + \alpha_z \alpha_y) p_y p_z (+\alpha_x \beta + \beta \alpha_x) m c p_x \\ &(+\alpha_y \beta + \beta \alpha_y) m c p_y (+\alpha_z \beta + \beta \alpha_z) m c p_z \end{aligned}$$

For this equation to be valid, it is necessary that

$$\alpha_x^2 = \alpha_y^2 = \alpha_z^2 = \beta^2 = 1, [\alpha_x, \alpha_y] = 0, [\alpha_y, \alpha_z] = 0$$

$$[\alpha, \alpha_z] = 0, [\alpha, \beta] = 0, [\alpha_y, \beta] = 0, [\alpha_z, \beta] = 0$$

It is obvious that the α 's and β 's can not be ordinary numbers. The anti-commuting nature of the α 's and β 's suggests that they have to be matrices. Since the square of these matrices are unit matrices, they are non-singular. As the α 's and β 's determine the Hamiltonian, they must be Hermitian.



5.4. show that the given matrix is not a constant of motion.

$$\sigma' = \begin{pmatrix} \sigma & 0 \\ 0 & \sigma \end{pmatrix}$$

Solution

The equation of motion of σ' in the Heisenberg picture is

$$i\hbar \frac{d\sigma'}{dt} = [\sigma', H]$$

Hence for σ' to be a constant of motion, σ'_x , σ'_y and σ'_z should commute with the Hamiltonian. Thus,

$$[\sigma'_x, H] = [\sigma'_x, c\alpha_x p_x + \beta mc^2]$$

Since σ'_x commutes with β ,

$$[\sigma'_x, H] = [\sigma'_x, c\alpha_x p_x] + [\sigma'_x, c\alpha_y p_y] + [\sigma'_x, c\alpha_z p_z]$$

Since,

$$[\sigma'_x, \alpha_x] = 0, [\sigma'_x, \alpha_y] = 2i\alpha_z, [\sigma'_x, \alpha_z] = -2i\alpha_y$$

$$[\sigma'_x, H] = 2ic(\alpha_z p_y - \alpha_y p_z) \neq 0$$

Hence the result.



5.5. Show that Dirac's Hamiltonian for a free particle commutes with the operator $\sigma \cdot p$, where p is the momentum operator and σ is the Pauli spin operator in the space of four component spinors.

Solution

Dirac's Hamiltonian for a free particle is

$$H = c(\sigma.p +) \beta mc^2$$

where,

$$\alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix} ; \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}$$

$$\alpha.p = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix} \cdot p = \begin{pmatrix} 0 & \sigma.p \\ \sigma.p & 0 \end{pmatrix}$$

$$\sigma.p = \sigma.pI = \begin{pmatrix} \sigma.p & 0 \\ 0 & \sigma.p \end{pmatrix}$$

$$\begin{aligned} [\sigma.p, H] &= [\sigma.p, c\alpha.p + \beta mc^2] = c([\sigma.p, \alpha.p] + [(\sigma.p), \beta mc^2]) \\ &= c \left[\begin{pmatrix} \sigma.p & 0 \\ 0 & \sigma.p \end{pmatrix}, \begin{pmatrix} 0 & \sigma.p \\ \sigma.p & 0 \end{pmatrix} \right] + mc^2 \left[\begin{pmatrix} \sigma.p & 0 \\ 0 & \sigma.p \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right] \\ &= 0 + 0 = 0 \end{aligned}$$

Hence the result.



5.9 Multiple Choice Questions

- The Position and Momentum operators are always
 - Commutative
 - Anti Commutative
 - Normalized
 - Orthogonal
- Expression for z-component of angular momentum is
 - $-i\hbar \frac{\partial}{\partial \phi}$
 - $-i\hbar \frac{\partial}{\partial \theta}$
 - $i\hbar \frac{\partial}{\partial \phi}$
 - $i\hbar \frac{\partial}{\partial \theta}$
- Components of angular momentum are
 - Orthogonal
 - Normal
 - Commute
 - Anti Commute
- Value of $L \times L$ is
 - 0
 - 1
 - $i\hbar L$
 - All of above
- The angular momentum of an isolated system is
 - Conserved
 - Non Conserved
 - Variable
 - None
- Spin does not depend on
 - S
 - m_s
 - spatial degrees of freedom
 - All of above
- For Hydrogen atom that are in ground state, the orbital angular momentum will be
 - 1
 - 2
 - 0
 - Unknown
- If azimuthal quantum number is 2, the number of values of the magnetic quantum number will be
 - 2
 - 3
 - 4
 - 5
- Square of angular momentum is
 - Hermitian
 - Anti hermitian
 - Linear
 - Projection Operator
- The square of angular momentum (J^2) commutes with
 - J_x
 - J_y
 - J_z
 - All of these

Answers

1	b	2	a	3	d	4	a	5	a
6	c	7	c	8	d	9	a	10	d

Chapter 6

Application to Quantum Mechanics

In this chapter, we will discuss the applications of time independent perturbation theory. In this regard, we will calculate the energy correction (due to the **fine structure** and the **Zeeman effect**) for the Hydrogen atom.

6.1 Fine Structure of Hydrogen Atom

In classical mechanics, scientists fail to explain splitting of H_α lines of hydrogen into doublet. In classical mechanics, spin concept was not have any grounds explanation. The splitting of states with the same n , is called fine structure. For hydrogen atom, the Hamiltonian is

$$H_0 = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \quad (6.1)$$

Eq.(6.1) consists of K.E of electron plus coulombic potential energy. But this is not quite the whole story. More significant is the fine structure of hydrogen atom which is due to two distinct mechanisms.

1. Spin-Orbit Coupling
2. Relativistic Correction

If we compare fine structure with Bohr energies (i.e. $E_n = \frac{-13.6}{n^2} \text{eV}$), fine structure is a tiny perturbation smaller by a factor of α^2 where α is,

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} = \frac{1}{137.036} \quad (6.2)$$

α is known as fine structure constant. Smaller still (by another factor of α) is called lamb shift. The lamb shift is associated with the quantization of electric field and smaller by yet another order of magnitude is the hyperfine structure. The hyperfine structure is due to the magnetic interaction between the spin dipole moments of electron and the proton.

6.2 Spin Orbit Coupling

Spin orbit coupling in Hydrogen arises from the interaction between the electron's spin magnetic moment $\mu_e = \frac{-eS}{m_e c}$ and the proton's orbital magnetic field $\vec{B}$ when proton is being seen by electron's perspective. Imagine an electron in orbit around the nucleus. From electron's point of view, the proton is circling around the electron (see Fig. (6.1)). This orbiting +ve charge of proton sets up a magnetic field $\vec{B}$ in the electron frame, which exerts a torque on the spinning electron, tending to align its magnetic moment μ along the direction of field $\vec{B}$.

The energy associated with its torque is given by hamiltonian

$$H = -\vec{\mu}_e \cdot \vec{B} \quad (6.3)$$

To find H we must find the magnetic field of proton ($\vec{B}$) and dipole moment of electron ($\vec{\mu}_e$).

Calculation of Magnetic field of proton ($\vec{B}$) and ($\vec{\mu}_e$)

If we consider proton (from the electron's perspective) as a continuous current loop, its magnetic field can be calculated from Biot-Savart law.

$$B = \frac{\mu_0 I}{2r} \quad (6.4)$$

Where $I = \frac{e}{T}$. Where e is the charge of proton and T is the period of orbit. Putting the value of I in Eq. (6.4).

$$B = \frac{\mu_0 \frac{e}{T}}{2r}$$

$$B = \frac{\mu_0 e}{2rT} \quad (6.5)$$

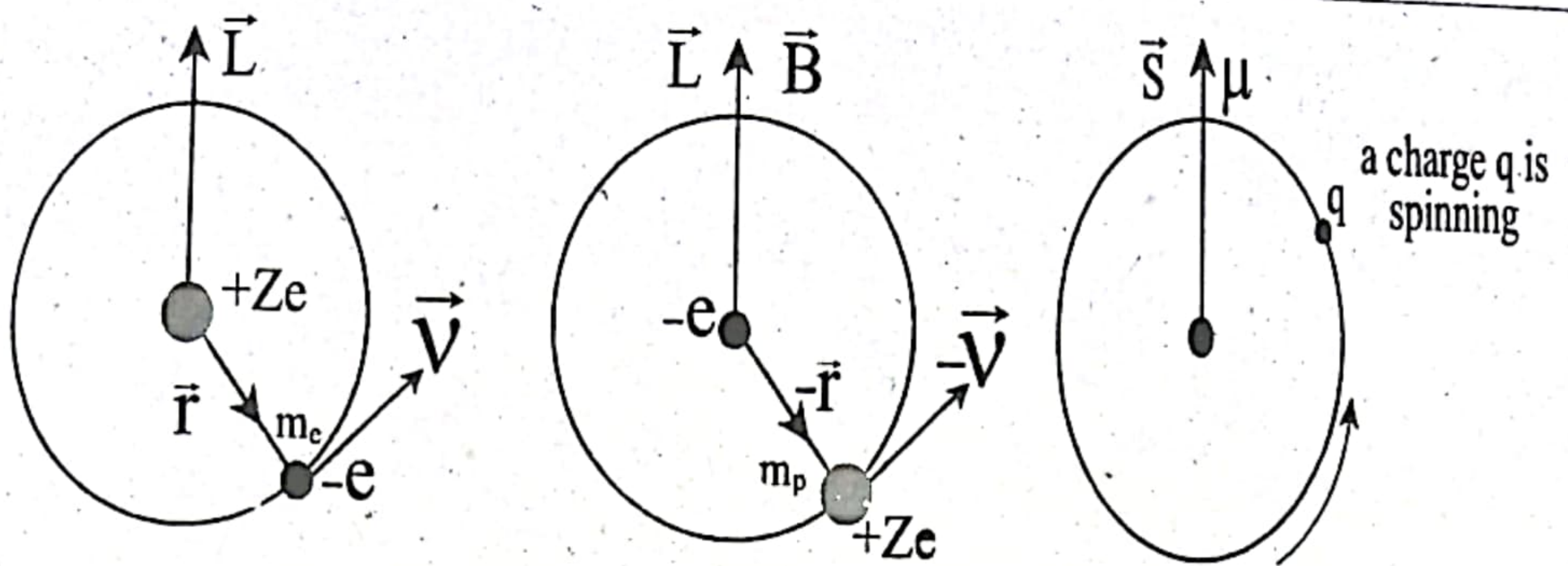


Fig. 6.1. Motion of electron w.r.t. nucleus and motion of nucleus w.r.t. electron (i.e. electron in rest frame.)

Calculation of T

The angular momentum of electron as electron is in orbit (in the rest frame of nucleus) is

$$L = mvr \quad (6.6)$$

As

$$\therefore S = vT \Rightarrow v = \frac{2\pi r}{T}$$

$$L = m \left(\frac{2\pi r}{T} \right) r$$

$$L = \frac{2\pi m r^2}{T}$$

$$T = \frac{2\pi m r^2}{L}$$

Moreover, $\vec{B}$ and $\vec{L}$ point in the same direction as shown in Fig. (6.1). So, Eq.(6.5) becomes;

$$\vec{B} = \frac{\mu_0 e}{2r \frac{2\pi m r^2}{L}}$$

$$\vec{B} = \frac{\mu_0 e \vec{L}}{4\pi m r^3} \quad (6.7)$$

We want ϵ_0 not μ_0 .

Calculation of μ_o

But,

$$c = \frac{1}{\sqrt{\epsilon_o \mu_o}} \Rightarrow c^2 = \frac{1}{\epsilon_o \mu_o}$$

$$\mu_o = \frac{1}{\epsilon_o c^2}$$

So Eq.(6.7) becomes;

$$\vec{B} = \frac{1}{\epsilon_o c^2} \frac{e \vec{L}}{4\pi m r^3}$$

$$\vec{B} = \frac{1}{4\pi \epsilon_o} \frac{e}{m c^2 r^3} \vec{L} \quad (6.8)$$

Now, as we know that the electron's spin magnetic dipole moment

$$\vec{\mu}_e = \frac{(-e)}{m} \vec{S} \quad (6.9)$$

Putting the value of $\vec{B}$ from Eq.(6.8) and $\vec{\mu}_e$ from Eq.(6.9) in Eq.(6.3) we get,

$$\hat{H} = - \left(-\frac{e}{m} \vec{S} \right) \cdot \left(\frac{1}{4\pi \epsilon_o} \frac{e}{m c^2 r^3} \right) (\vec{L})$$

$$\hat{H} = \left(\frac{e^2}{4\pi \epsilon_o} \right) \left(\frac{1}{m^2 c^2 r^3} \right) (\vec{S} \cdot \vec{L}) \quad (6.10)$$

This analysis was made in rest frame of electron, but that's not an inertial system because electron accelerates while moving around the nucleus. We can apply an appropriate kinetic correction, which is known as Thomas precession¹. For this purpose, we multiply Eq. (6.10) by $\frac{1}{2}$

$$\hat{H}_{SO} = \frac{1}{2} \hat{H}$$

$$\hat{H}_{SO} = \frac{1}{2} \left(\frac{e^2}{4\pi \epsilon_o} \right) \left(\frac{1}{m^2 c^2 r^3} \right) (\vec{S} \cdot \vec{L})$$

¹ Concept:- The precession of $\vec{\mu}_e$ is a relativistic effect which occurs even in the absence of $\vec{B}$. The transformation back to the rest frame of nucleus leads to a reduction of energy by factor 2.

$$\hat{H}_{SO} = \left(\frac{e^2}{8\pi\epsilon_0} \right) \left(\frac{1}{m^2 c^2 r^3} \right) (\vec{S} \cdot \vec{L}) \quad (6.11)$$

This is the spin orbit interaction. So Hamiltonian becomes after considering spin-orbit interaction is

$$\hat{H} = \hat{H}_0 + \hat{H}_{SO} \quad (6.12)$$

Calculation of $\vec{L} \cdot \vec{S}$

In quantum mechanics, in the presence of spin orbit coupling, the Hamiltonian does not commute or diagonalized with $\vec{L}$ and $\vec{S}$, so the spin and orbital angular momenta are not separately conserved. However $\hat{H}_{SO}$ commutes with L^2 , S^2 and the total angular momentum $\vec{J} = \vec{L} + \vec{S}$. The eigen states of $\vec{L}$ and $\vec{S}$ are not good states to be used in perturbation theory, but the eigen states $|nljm\rangle$ of L^2 , S^2 , J^2 and J_z are good to be used in the perturbation theory. Now,

$$\begin{aligned} J^2 &= \vec{J} \cdot \vec{J} = (\vec{L} + \vec{S}) \cdot (\vec{L} + \vec{S}) \\ J^2 &= L^2 + S^2 + 2(\vec{L} \cdot \vec{S}) \\ J^2 - L^2 - S^2 &= 2(\vec{L} \cdot \vec{S}) \\ 2(\vec{L} \cdot \vec{S}) &= J^2 - L^2 - S^2 \\ (\vec{L} \cdot \vec{S}) &= \frac{1}{2} (J^2 - L^2 - S^2) \end{aligned}$$

The eigen values of $\vec{L} \cdot \vec{S}$ are.

$$\begin{aligned} \vec{L} \cdot \vec{S} &= \frac{1}{2} [j(j+1)\hbar^2 - \ell(\ell+1)\hbar^2 - s(s+1)\hbar^2] \\ \vec{L} \cdot \vec{S} &= \frac{\hbar^2}{2} [j(j+1) - \ell(\ell+1) - s(s+1)] \\ \vec{L} \cdot \vec{S} &= \frac{\hbar^2}{2} \left[j(j+1) - \ell(\ell+1) - \frac{1}{2} \left(\frac{1}{2} + 1 \right) \right] \\ \vec{L} \cdot \vec{S} &= \frac{\hbar^2}{2} \left[j(j+1) - \ell(\ell+1) - \frac{3}{4} \right] \end{aligned} \quad (6.13)$$

Calculation of $\frac{1}{r^3}$

We know that,

$$\begin{aligned}\left\langle \frac{1}{r} \right\rangle &= \frac{1}{n^2 a} \\ \left\langle \frac{1}{r^2} \right\rangle &= \frac{1}{\left(\ell + \frac{1}{2}\right) n^3 a^2} \\ \left\langle \frac{1}{r^3} \right\rangle &= \frac{1}{\ell \left(\ell + \frac{1}{2}\right) (\ell + 1) n^3 a^3}\end{aligned}\quad (6.14)$$

Putting the value of $\vec{L} \cdot \vec{S}$ from Eq.(6.13) and $\frac{1}{r^3}$ from Eq.(6.14) in Eq.(6.11)

$$\begin{aligned}E_{so}^1 &= \langle \hat{H}_{SO} \rangle = \left(\frac{e^2}{8\pi\epsilon_0} \right) \cdot \left(\frac{1}{m^2 c^2} \right) \frac{\hbar^2}{2} \frac{[j(j+1) - \ell(\ell+1) - \frac{3}{4}]}{\ell(\ell + \frac{1}{2})(\ell + 1) n^3 a^3} \\ &= \frac{1}{2a} \left(\frac{e^2}{4\pi\epsilon_0 n^2} \right) \cdot \left(\frac{\hbar^2}{m^2 c^2 a^2} \right) \frac{1}{n} \frac{[j(j+1) - \ell(\ell+1) - \frac{3}{4}]}{\ell(\ell + 1)(2\ell + 1)}\end{aligned}$$

As also we know that

$$a = \frac{4\pi\epsilon_0 \hbar^2}{m e^2} \Rightarrow a^3 = \frac{64\pi^3 \epsilon_0^3 \hbar^6}{m^3 e^6} \quad \text{and} \quad \alpha = \frac{\hbar}{m c a} = \frac{1}{137}, \quad (6.15)$$

and energy of electron

$$\begin{aligned}E_n^o &= \left[-\frac{m}{2\hbar^2} \frac{e^4}{16\pi^3 \epsilon_0^2} \right] \frac{1}{n^2} \\ E_n^o &= -\frac{E_o}{n^2} = -\frac{e^2}{4\pi\epsilon_0 2a n^2}\end{aligned}$$

$$E_{so}^1 = \frac{|E_n^o| \alpha^2}{n} \left[\frac{[j(j+1) - \ell(\ell+1) - \frac{3}{4}]}{\ell(\ell + 1)(2\ell + 1)} \right] \quad (6.16)$$

6.3 Relativistic Correction

Now, we are considering the relativistic speed of the electron in its orbit. The first term in the Hamiltonian is supposed to represent classical kinetic energy T .

$$T = \frac{1}{2} m v^2 = \frac{m^2 v^2}{2m} = \frac{P^2}{2m} \quad (6.17)$$

$$P = -i\hbar\nabla = -i^2 \frac{\hbar}{i} \nabla = \frac{\hbar}{i} \nabla \quad (6.18)$$

Putting the value of P in Eq. (6.17)

$$T = \frac{\left(\frac{\hbar}{i}\nabla\right)^2}{2m} = -\frac{\hbar^2\nabla^2}{2m} \quad (6.19)$$

The relativistic formula for kinetic energy is

$$T = \frac{mc^2}{\sqrt{1 - \left(\frac{v}{c}\right)^2}} - mc^2 \quad (6.20)$$

First term is total relativistic energy and second term is the rest mass energy. The difference is due to motion of electron. We need to express T in terms of the relativistic momentum.

$$p = \frac{mv}{\sqrt{1 - \left(\frac{v}{c}\right)^2}} \Rightarrow p^2 c^2 = \frac{m^2 v^2 c^2}{1 - \frac{v^2}{c^2}} \quad (6.21)$$

Adding $m^2 c^4$ on both sides of Eq.(6.21)

$$\begin{aligned} p^2 c^2 + m^2 c^4 &= m^2 c^4 + \frac{m^2 v^2 c^2}{1 - \frac{v^2}{c^2}} \\ &= \frac{m^2 c^4 \left(1 - \frac{v^2}{c^2}\right) + m^2 v^2 c^2}{1 - \left(\frac{v}{c}\right)^2} \\ &= \frac{m^2 c^4 - m^2 c^4 \frac{v^2}{c^2} + m^2 v^2 c^2}{1 - \left(\frac{v}{c}\right)^2} \\ &= \frac{m^2 c^4 - m^2 c^2 v^2 + m^2 v^2 c^2}{1 - \left(\frac{v}{c}\right)^2} \\ p^2 c^2 + m^2 c^4 &= \frac{m^2 c^4}{1 - \left(\frac{v}{c}\right)^2} \end{aligned} \quad (6.22)$$

But from Eq.(6.20)

$$T + mc^2 = \frac{mc^2}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

Squaring both side of above equation.

$$(T + mc^2)^2 = \frac{(mc^2)^2}{1 - \left(\frac{v}{c}\right)^2} \quad (6.23)$$

Comparing Eqs. (6.22) & (6.23), we get,

$$p^2c^2 + m^2c^4 = (T + mc^2)^2$$

Taking square root on both sides.

$$\begin{aligned} \sqrt{p^2c^2 + m^2c^4} &= T + mc^2 \\ T + mc^2 &= \sqrt{p^2c^2 + m^2c^4} \\ T &= \sqrt{p^2c^2 + m^2c^4} - mc^2 \end{aligned}$$

This relativistic equation for kinetic energy reduces to classical result $\left(T = \frac{p^2}{2m}\right)$, in the non relativistic limit $p \ll mc$. Expanding in powers of the small number $\left(\frac{p}{mc}\right)$, we have

$$\begin{aligned} T &= \sqrt{p^2c^2 + m^2c^4} - mc^2 \\ T &= \sqrt{m^2v^2c^2 + m^2c^4} - mc^2 \\ T &= \sqrt{m^2c^4 \left(\frac{v^2}{c^2} + 1\right)} - mc^2 \\ T &= mc^2 \sqrt{1 + \frac{v^2}{c^2}} - mc^2 \end{aligned}$$

Multiplying and dividing by m^2 2nd term of square root.

$$\begin{aligned} T &= mc^2 \sqrt{1 + \frac{m^2v^2}{m^2c^2}} - mc^2 \\ T &= mc^2 \sqrt{1 + \frac{p^2}{m^2c^2}} - mc^2 \\ T &= mc^2 \sqrt{1 + \left(\frac{p}{mc}\right)^2} - mc^2 \end{aligned}$$

$$\begin{aligned}
 T &= mc^2 \left[\left\{ 1 + \left(\frac{p}{mc} \right)^2 \right\}^{\frac{1}{2}} - 1 \right] \\
 T &= mc^2 \left[1 + \frac{1}{2} \left(\frac{p}{mc} \right)^2 - \frac{1}{8} \left(\frac{p}{mc} \right)^4 - 1 \right] \\
 T &= mc^2 \left[\frac{1}{2} \left(\frac{p}{mc} \right)^2 - \frac{1}{8} \left(\frac{p}{mc} \right)^4 \right] \\
 T &= \frac{mc^2 p^2}{2m^2 c^2} - \frac{mc^2 p^4}{8m^4 c^4} \\
 T &= \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2}
 \end{aligned}$$

The lowest order relativistic correction to Hamiltonian is then

$$\hat{H}_R = -\frac{p^4}{8m^3 c^2} \quad (6.24)$$

When this term is included, the Hydrogen's Hamiltonian becomes $\hat{H} = \hat{H}_0 + \hat{H}_R$. In the first order perturbation theory, the correction to E_R is given by the expectation value of $\hat{H}_R$

$$\begin{aligned}
 E_R^1 &= \langle \psi | H_R | \psi \rangle \\
 E_R^1 &= \langle H_R \rangle \\
 E_R^1 &= \left\langle -\frac{p^4}{8m^3 c^2} \right\rangle \\
 E_R^1 &= -\frac{1}{8m^3 c^2} \langle p^4 \rangle \\
 E_R^1 &= -\frac{1}{8m^3 c^2} \langle \psi | p^4 | \psi \rangle \\
 E_r^1 &= -\frac{1}{8m^3 c^2} \langle p^2 \psi | p^2 \psi \rangle
 \end{aligned} \quad (6.25)$$

We know that, the energy of unperturbed state is

$$E = K.E + P.E$$

$$E = \frac{p^2}{2m} + V(r)$$

$$E - V(r) = \frac{p^2}{2m}$$

$$2m(E - V(r)) = p^2$$

$$p^2 = 2m(E - V(r))$$

Multiplying above equation by $|\psi\rangle$,

$$p^2|\psi\rangle = 2m(E - V(r))|\psi\rangle$$

So, Eq.(6.25) becomes;

$$E_R^1 = -\frac{1}{8m^3c^2} \langle [2m(E - V(r)) \{2m(E - V(r))\}] \rangle \langle \psi|\psi \rangle$$

$$E_R^1 = -\frac{1}{8m^3c^2} [4m^2 \langle (E - V(r))^2 \rangle] \quad \because \langle \psi|\psi \rangle = 1$$

$$E_R^1 = -\frac{1}{2mc^2} [E^2 - 2E\langle V(r) \rangle + \langle V(r)^2 \rangle] \quad (6.26)$$

This is entirely a general relation. In case of hydrogen for which the P.E is;

$$V(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \quad \text{and} \quad E = E_n^o \quad \text{Bohr energy of the state} \quad (6.27)$$

So Eq.(6.26) becomes

$$E_R^1 = -\frac{1}{2mc^2} \left[E_n^{o2} + 2E_n^o \left(\frac{e^2}{4\pi\epsilon_0} \right) \left\langle \left(\frac{1}{r} \right) \right\rangle + \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \left\langle \left(\frac{1}{r} \right)^2 \right\rangle \right] \quad (6.28)$$

As we know, the expectations values of $\frac{1}{r}$ and $\frac{1}{r^2}$ in the (unperturbed) state $|\psi_{nlm}\rangle$

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a}, \quad (6.29)$$

where a is the Bohr radius

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(l + \frac{1}{2}) n^3 a^2}$$

So, Eq.(6.28) becomes;

$$E_R^1 = -\frac{1}{2mc^2} \left[E_n^{o2} + 2E_n^o \left(\frac{e^2}{4\pi\epsilon_o} \right) \left(\frac{1}{n^2a} \right) + \left(\frac{e^2}{4\pi\epsilon_o} \right)^2 \left(\frac{1}{(l + \frac{1}{2}) n^3 a^2} \right) \right] \quad (6.30)$$

Eliminating E_n^o by putting $E_n^o = -\frac{e^2}{8\pi\epsilon_o a n^2}$, We get

$$E_R^1 = -\frac{1}{2mc^2} \left[\frac{e^4}{64\pi^2\epsilon_o^2 a^2 n^4} + 2 \left(-\frac{e^2}{8\pi\epsilon_o a n^2} \right) \left(\frac{e^2}{4\pi\epsilon_o n^2 a} \right) + \frac{e^4}{16\pi^2\epsilon_o^2 a^2} \left(\frac{1}{(l + \frac{1}{2}) n^3} \right) \right]$$

$$E_R^1 = -\frac{1}{2mc^2} \left[\frac{e^4}{64\pi^2\epsilon_o^2 a^2 n^4} - \frac{e^4}{16\pi^2\epsilon_o^2 a^2 n^4} + \frac{e^4}{16\pi^2\epsilon_o^2 a^2 n^3} \left(\frac{2}{2l+1} \right) \right]$$

$$E_R^1 = -\frac{1}{2mc^2} \left[\frac{-3e^4}{16\pi^2\epsilon_o^2 a^2 n^4} + \frac{e^4}{16\pi^2\epsilon_o^2 a^2 n^3} \left(\frac{2}{2l+1} \right) \right]$$

$$E_R^1 = -\frac{1}{2mc^2} \cdot \frac{e^4}{64\pi^2\epsilon_o^2 a^2 n^4} \left[-3 + \frac{64n}{16} \left(\frac{2}{2l+1} \right) \right]$$

$$E_R^1 = -\left(\frac{e^2}{8\pi\epsilon_o a n^2} \right) \left(\frac{e^2}{4mc^2\pi\epsilon_o a} \right) \frac{1}{4n^2} \left(\frac{8n}{2l+1} - 3 \right)$$

$$E_R^1 = -\frac{\alpha^2 |E_n^o|}{4n^2} \left(\frac{8n}{2l+1} - 3 \right) \quad (6.31)$$

Note that the spin-orbit (Eq.(6.16)) and relativistic corrections (Eq.(6.31)) have the same order of magnitude, 10^{-3} eV, since $\alpha^2 |E_n^o| \simeq 10^{-3}$ eV.

6.4 Fine Structure

Adding the two equations Eq.(6.16) and Eq.(6.31) together, we get complete fine structure formula

$$E_{FS}^1 = E_R^1 + E_{SO}^1$$

$$E_{FS}^1 = -\frac{\alpha^2 |E_n^o|}{4n^2} \left[\frac{8n}{2l+1} - 3 \right] + \alpha^2 \frac{|E_n^o|}{n} \left[\frac{j(j+1) - \ell(\ell+1) - \frac{3}{4}}{\ell(\ell+1)(2l+1)} \right] \quad (6.32)$$

Where $j = \ell \pm \frac{1}{2}$, if we take $j = \ell + \frac{1}{2}$ or $j = \ell - \frac{1}{2}$ answer will be same for fine structure correction. So,

$$j = l + \frac{1}{2}$$

$$l = j - \frac{1}{2}$$

Putting value of $l = j - \frac{1}{2}$ in Eq.(6.32). We get,

$$E_{FS}^1 = \frac{\alpha^2 |E_n^o|}{4n^2} \left[-\frac{8n}{2j-1+1} + 3 + \frac{4n j(j+1) - 4n (j - \frac{1}{2})(j + \frac{1}{2}) - 3n}{(j - \frac{1}{2})(j + \frac{1}{2})(2j - 1 + 1)} \right]$$

$$E_{FS}^1 = \frac{\alpha^2 |E_n^o|}{4n^2} \left[-\frac{4n}{j} + 3 + \frac{4n j^2 + 4nj - 4n j^2 + 4n \frac{j}{2} - 4n \frac{j}{2} + 4n \cdot \frac{1}{4} - 3n}{(2j-1)(j + \frac{1}{2})2j} \right]$$

$$E_{FS}^1 = \frac{\alpha^2 |E_n^o|}{4n^2} \left[-\frac{4n}{j} + 3 + \frac{4nj - 2n}{(j - \frac{1}{2})(j + \frac{1}{2})2j} \right]$$

$$E_{FS}^1 = \frac{\alpha^2 |E_n^o|}{4n^2} \left[-\frac{4n}{j} + 3 + \frac{2n(2j-1)}{2(j - \frac{1}{2})(j + \frac{1}{2})j} \right]$$

$$E_{FS}^1 = \frac{\alpha^2 |E_n^o|}{4n^2} \left[-\frac{4n}{j} + 3 + \frac{2n}{j(j + \frac{1}{2})} \right]$$

$$E_{FS}^1 = \frac{\alpha^2 |E_n^o|}{4n^2} \left[+3 + \left(-\frac{4n(j + \frac{1}{2}) + 2n}{j(j + \frac{1}{2})} \right) \right]$$

$$E_{FS}^1 = \frac{\alpha^2 |E_n^o|}{4n^2} \left[+3 + \frac{-4nj - 2n + 2n}{j(j + \frac{1}{2})} \right]$$

$$E_{FS}^1 = \frac{\alpha^2 |E_n^o|}{4n^2} \left[+3 - \frac{4nj}{j(j + \frac{1}{2})} \right]$$

$$E_{FS}^1 = \frac{\alpha^2 |E_n^o|}{4n^2} \left[+3 - \frac{4n}{(j + \frac{1}{2})} \right]$$

(6.33)

Combining Eq.(6.33) with the *Bohr formula*, we obtain the grand result for the energy levels of hydrogen, including fine structure.

$$E_{nj} = E_n^0 + E_{FS}^1$$

$$E_{nj} = E_n^0 \left[1 + \frac{\alpha^2}{4n^2} \left(3 - \frac{4n}{(j + \frac{1}{2})} \right) \right]$$
(6.34)

Unlike E_n^o , which is degenerate in ℓ , each energy level E_{nj} is split into two levels $E_{n(\ell \pm \frac{1}{2})}$, since for a given value of ℓ there are two values of j ; $j = \ell \pm \frac{1}{2}$.

6.5 Zeeman effect

The Zeeman effect, named after the Dutch physicist Pieter Zeeman, is the effect of splitting of a spectral line of an atomic spectrum into several components in the presence of a magnetic field (B_{ext}). It is analogous to the Stark effect, the splitting of a spectral line into several components in the presence of an electric field. The Zeeman effect is a strong confirmation of space quantization.

Historically, one distinguishes between the normal and an anomalous Zeeman effect. In normal Zeeman effect (spin of electron = 0), each energy level splits into an odd number $(2\ell + 1)$ of equally spaced levels, disagree with the experimental observations

In anomalous Zeeman effect (spin of electron is considered), each energy level splits into an even number $(2j + 1)$ of unequally spaced energy levels, agree with the experimental findings.

For single electron system, the interaction of $\vec{B}_{ext}$ with the electron's orbital and spin magnetic dipole moments (see Fig. (6.2)), $\vec{\mu}_L$ and $\vec{\mu}_S$, give rise to two energy terms, $-\vec{\mu}_L \cdot \vec{B}_{ext}$ and $-\vec{\mu}_S \cdot \vec{B}_{ext}$

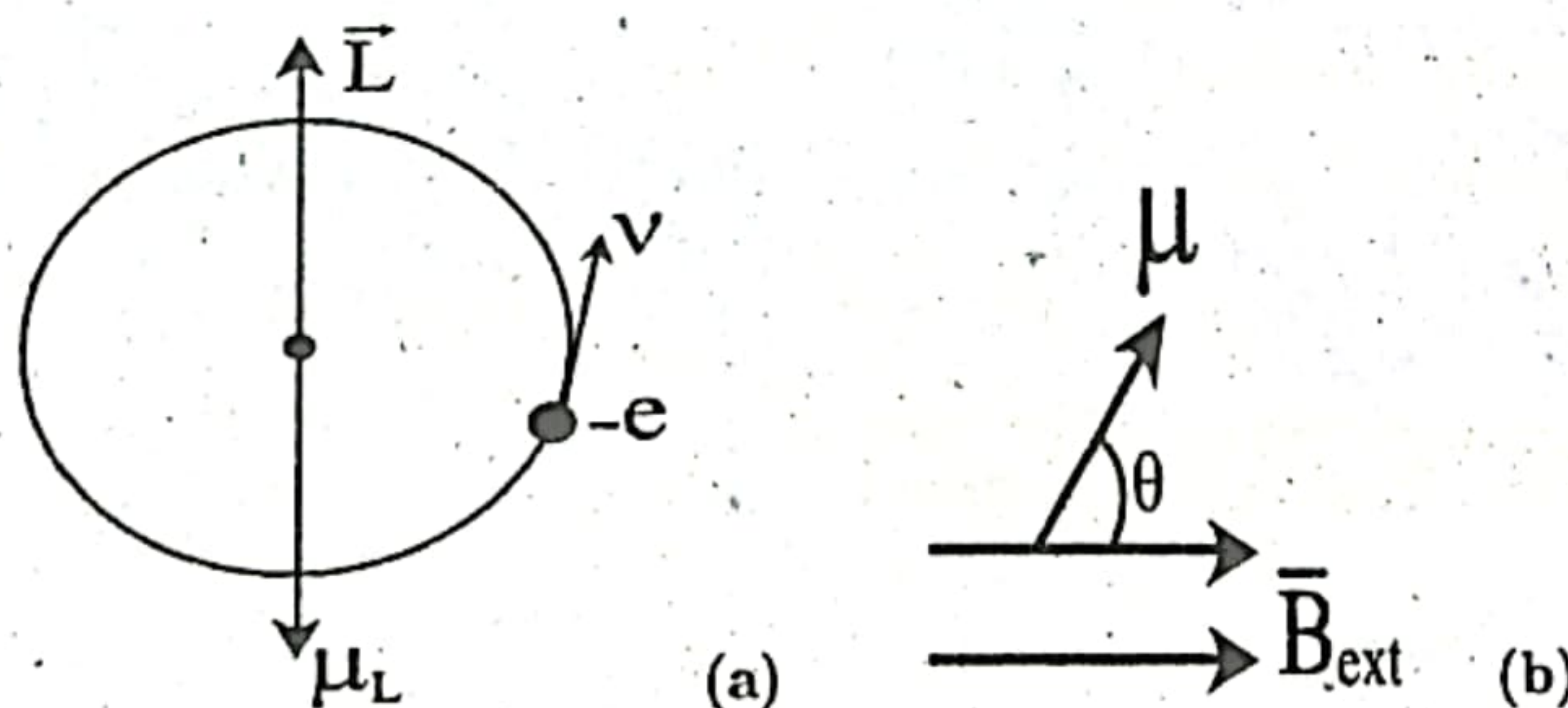


Fig. 6.2. (a) Motion of electron and direction of magnetic moment. (b) Direction of magnetic moments and magnetic field (external).

Whose some we call the zeeman energy (Perturbation)

$$H_Z = -\vec{\mu}_L \cdot \vec{B}_{ext} - \vec{\mu}_S \cdot \vec{B}_{ext}$$

$$(\vec{\mu}_L + \vec{\mu}_S) \cdot \vec{B}_{ext} \quad (6.35)$$

where,

$$\vec{\mu}_L = \frac{-e}{2m} \vec{L} \quad ; \quad \vec{\mu}_S = \frac{-e}{m} \vec{S}$$

Negative sign means that μ is always opposite to $\vec{S}$ or $\vec{L}$ and is a consequence of the negative charge of electron.

$$H_z = \left(\frac{e}{2m} \vec{L} + \frac{e}{m} \vec{S} \right) \cdot \vec{B}_{ext}$$

$$H_z = \frac{e}{2m} (L + 2S) \cdot B_{ext} \quad (6.36)$$

The Zeeman splitting depends on strength of external magnetic field ($\vec{B}_{ext}$) in comparison with internal field (fine structure). So total hamiltonian of one electron system is,

$$H = H_0 + H_{fs} + H_z$$

Like H_{fs} , the correction due to H_z is expected to be small compared to H_0 , hence it can be treated as perturbation. Now, we discuss three cases,

1. Weak - field Zeeman effect ($B_{ext} \ll B_{int}$), then fine structure dominates and H_z can be treated as a small perturbation.
2. Strong field Zeeman effect ($B_{ext} \gg B_{int}$), then Zeeman effect dominates and fine structure becomes small perturbation.
3. Intermediate zone ($B_{ext} = B_{int}$), so we need the full machinery of degenerate perturbation theory.

1. Weak Field Zeeman Effect

In ($B_{ext} \ll B_{int}$), the fine structure perturbation dominates; the good quantum numbers are n, l, j and m_j (but not m_l and m_s because in the presence of spin-orbit coupling, L and S are not separately conserved) makes the eigen state ($|nljm_j\rangle$) of H_{fs} (i.e. $H = H_0 + H_{fs} + H_z$). In first order perturbation theory, the Zeeman correction to energy is

$$E_z^1 = \langle nljm_j | H_z | nljm_j \rangle$$

Using Eq.(6.36) and normalized condition of eigen state

$$\begin{aligned}
&= \frac{e}{2m} \langle \vec{L} + 2\vec{S} \rangle \cdot \vec{B}_{ext} \\
&= \frac{e}{2m} \vec{B}_{ext} \langle \vec{J} + \vec{S} \rangle \\
&\therefore (\vec{L} + \vec{S} = \vec{J})
\end{aligned} \tag{6.37}$$

Unfortunately we don't know the expectation value of $\vec{S}$. $[H_{fs}, \vec{S}] \neq 0$ so we write $\vec{S}$ in terms of J^2 , L^2 , S^2 . $\vec{L} + \vec{S} = \vec{J}$ is the total angular momentum, which is always constant (if external torque is zero) i.e. $\vec{L}$ and $\vec{S}$ precess rapidly about $\vec{J}$. The average value of $\vec{S}$ is projection of $\vec{S}$ along $\vec{J}$.

$$\begin{aligned}
S_{av} &= \vec{S} \cdot \hat{J} \\
S_{av} &= \frac{\vec{S} \cdot \vec{J}}{J} \\
\vec{S}_{av} &= \frac{\vec{S} \cdot \vec{J}}{J} \hat{J} \\
\vec{S}_{av} &= \frac{\vec{S} \cdot \vec{J}}{J^2} \vec{J}
\end{aligned}$$

Now, $\vec{J} = \vec{L} + \vec{S}$ and $l = j - s$ on squaring,

$$L^2 = (\vec{J} - \vec{S}) \cdot (\vec{J} - \vec{S}) = J^2 + S^2 - 2\vec{S} \cdot \vec{J}$$

$$\langle J^2 \rangle = \hbar^2 j(j+1), \quad \langle S^2 \rangle = \hbar^2 s(s+1), \quad \langle L^2 \rangle = \hbar^2 l(l+1)$$

$$\langle J \rangle = m_j \hbar$$

So Eq.(6.37) becomes

$$E_z^1 = \frac{e}{2m} \vec{B}_{ext} \cdot \left\langle \vec{J} + \left(\frac{\vec{S} \cdot \vec{J}}{J^2} \right) \vec{J} \right\rangle$$

$$F_z^1 = \frac{e}{2m} \vec{B}_{ext} \cdot \left\langle 1 + \left(\frac{\vec{S} \cdot \vec{J}}{J^2} \right) \right\rangle \langle \vec{J} \rangle$$

$$F_z^1 = \frac{e}{2m} B_{ext} \cdot \left[1 + \frac{j(j+1) - l(l+1) + \frac{3}{4}}{2j(j+1)} \right] m_j \hbar$$

Where

$$\begin{aligned}
 &= s(s+1) = \frac{1}{2} \left(\frac{1}{2} + 1 \right) \\
 &= \frac{1}{2} \left(\frac{3}{2} \right) = \frac{3}{4}
 \end{aligned}$$

Bohr Magneton = $\mu_B = 5.788 \times 10^{-5} \text{ eV/T}$. The term in square bracket is called Lande g -factor. Also, we may choose the z -axis to lie along $\vec{B}_{ext}$, then

$$E_z^1 = \mu_B B_{ext} m_j g_j$$

The total energy is the sum of the fine structure and Zeeman contribution. For example, Ground state ($n = 1, l = 0, j = s = 1/2$ and therefore $g_j = 2$) splits into two levels.

$$-13.6 \text{ eV} \left(1 + \frac{\alpha^2}{4} \right) \pm \mu_B B_{ext}$$

Energy of hydrogen atom in weak B_{ext}

$$E_{nj} = E_n^o + E_{fs}^1 + E_z^1$$

$$E_{nj} = E_n^o + \frac{\alpha^2 E_n^o}{4} \left(\frac{4n}{j + \frac{1}{2}} - 3 \right) + \mu_B B_{ext} m_j g_j$$

2. Strong Field Zeeman Effect

In $B_{ext} \gg B_{int}$, Zeeman effect perturbation dominates; the good quantum numbers are n, l, m_l and m_s (but not j and m_j because in the presence of external torque, the total angular momentum J is not conserved, whereas $(L)L_z$ and $(S)S_z$ are) makes the eigen state ($|nlm_l m_s\rangle$) of H_z . This effect is called paschen-back effect.

Here H_{fs} is neglected. So

$$H = H_o + H_z$$

The Zeeman Hamiltonian is,

$$H_z = \frac{e}{2m} \vec{B}_{ext} (\vec{L} + 2\vec{S})$$

$$E_z^1 = \langle nlm_l m_s | \frac{e}{2m} \vec{B}_{ext} (\vec{L} + 2\vec{S}) | nlm_l m_s \rangle$$

$$\begin{aligned}
&= \frac{e}{2m} \vec{B}_{ext} \langle \vec{L} + 2\vec{S} \rangle \\
\therefore \langle \vec{L} \rangle &= m_l \hbar, \quad \langle \vec{S} \rangle = m_s \hbar \\
&= \frac{e\hbar}{2m} B_{ext} (m_l + 2m_s) \\
&= \mu_B B_{ext} (m_l + 2m_s)
\end{aligned}$$

Total energy is.

$$\begin{aligned}
E_{nlm_l m_s} &= E_n^0 + \mu_B B_{ext} (m_l + 2m_s) \\
E_{nlm_l m_s} &= -\frac{13.6 \text{ eV}}{n^2} + \mu_B B_{ext} (m_l + 2m_s)
\end{aligned}$$

Here energy levels E_n^0 are shifted by an amount $\Delta E = \mu_B B_{ext} (m_l + 2m_s)$ known as paschan-back shift.

3. Intermediate Field Zeeman Effect

In the intermediate region, neither H_z nor H_{fs} dominates, and we must treat the two on an equal footing, as perturbations to the Bohr Hamiltonian.

$$H = H_z + H_{fs}$$

In this region, we use machinery of eigen value matrices which is difficult one so leave it. The Zeeman effect is very important in magnetic resonance imaging (MRI).

6.6 Review Questions

- 6.1 Why spin-orbit interaction arises ?
- 6.2 Define and explain the role of fine structure constant (α) in energy splitting.
- 6.3 Explain the spin-orbit coupling and consequences originating from this effect?
- 6.4 Differentiate between normal and anomalous Zeeman effect.
- 6.5 Define Stark effect.
- 6.6 Give the physical interpretation of the equation $\hat{H}_{SO} = \frac{e^2}{2m_e^2 c^2 r^3} \hat{S} \cdot \hat{L}$
- 6.7 What is meant by fine structure and hyperfine structure of hydrogen atom?
- 6.8 Draw the energy levels for s and p orbitals by using the $\Delta E = B\mu_B(m_l + 2m_s)$
- 6.9 Draw the energy levels for $2P_{3/2}$ by using the $E_Z^{(1)} = B\mu_B g_j m_j$ if $g_j = 4/3$.
- 6.10 Define the possible applications of Zeeman effect.



6.7 Solved Problems

- 6.1. Draw the energy levels, including the spin orbit interaction for $n = 3$ and $n = 2$ states of hydrogen atom and calculate the spin orbit doublet separation of the $2P$, $3P$ and $3d$ states. The Rydberg constant of hydrogen is $1.097 \times 10^7 m^{-1}$.

Solution

As we know that the energy level for $n = 3$ and $n = 2$ states of hydrogen ($Z = 1$), including the spin orbit interaction.

The doublet separation

$$\Delta E = \frac{Z^4 \alpha^2 R}{n^3(l+1)}$$

For the $2P$ state, $n = 2, l = 1$, and hence

$$(\Delta E)_{2P} = \frac{(1/137)^2 (1.097 \times 10^7 m^{-1})}{8 \times 2} = 36.53 m^{-1}$$

For $3P$ state $n = 3, l = 1$ and so

$$(\Delta E)_{3P} = \frac{(1/137)^2 (1.097 \times 10^7 m^{-1})}{27 \times 2} = 10.82 m^{-1}$$

For the 3d state $n = 3, l = 2$ and, therefore,

$$(\Delta E)_{3d} = \frac{(1/137)^2 (1.097 \times 10^7 m^{-1})}{27 \times 2 \times 3} = 3.61 m^{-1}$$

Note: The doublet separation decreases as l increases. The 2P doublet separation is greater than the 3P doublet which will be greater than the 4P separation (if evaluated), and so on. The d electron doublet splitting are also similar.



6.2. The spin orbit interaction energy

$$E_{SO} = \frac{z^4 \alpha^4 mc^2}{2n^3} \frac{j(j+1) - l(l+1) - s(s+1)}{l(l+1)(2l+1)}$$

Calculate the doublet separation ΔE_{SO} of states with the same n and l . Apply the result to the 2P state of hydrogen and obtain the doublet separation in units of eV.

Solution

For a given value of l , j can have the values $j = l + (1/2)$ and $j = l - (1/2)$. The difference in energy between these two is the doublet separation ΔE_{SO} . Hence,

$$\begin{aligned} \Delta E_{SO} &= \frac{z^4 \alpha^4 mc^2}{2n^3 l(l+1)(2l+1)} \left[\left(l + \frac{1}{2} \right) \left(l + \frac{3}{2} \right) - \left(l - \frac{1}{2} \right) \left(l + \frac{1}{2} \right) \right] \\ &= \frac{z^4 \alpha^4 mc^2 (2l+1)}{2n^3 l(l+1)(2l+1)} = \frac{z^4 \alpha^4 mc^2}{2n^3 l(l+1)} \end{aligned}$$

For the 2P state of hydrogen, $n = 2, l = 1, z = 1$. So,

$$\begin{aligned} \Delta E_{SO} &= \frac{(9.1 \times 10^{-31} kg)(3 \times 10^8 ms^{-1})}{(137)^4 \times 2 \times 2^3 \times 2} = 7.265 \times 10^{-24} J \\ &= \frac{1.765 \times 10^{-24} J}{1.6 \times 10^{-19} J/eV} = 4.5 \times 10^{-5} eV \end{aligned}$$



6.8 Multiple Choice Questions

- Application of Barrier Tunneling are
a) Radioactive Decay b) Semiconductor Devices c) Both a and b d) none
- The energy of free particle in 3D is
a) Triply degenerate b) Non degenerate c) Infinitely Degenerate d) None
- The Centrifugal potential depends on — — — quantum number
a) Orbital b) Magnetic c) Principle d) All of above
- Three dimensional problems often exhibit degeneracy, which occur whenever — — — is symmetric
a) Eigen value b) Wavefunction c) Potential d) None
- Value of square of any Pauli spin matrix is — — — matrix
a) Null b) Diagonal c) Identity d) None
- As the particle angular momentum increases, the particle becomes less and less
a) Repulsive b) unbound c) bound d) Both a and b
- Eigen values of square of spin angular momentum are
a) $s(s+1)2\hbar^2$ b) $s(2s+1)\hbar^2$ c) $s(s+1)\hbar^2$ d) $s(2s+1)\hbar^2$
- Radial equation for central potential depends on — — — — — quantum number
a) Azimuthal b) Magnetic c) Spin d) None
- The hamiltonian of rigid rotator
a) $\hat{H} = \frac{\hat{L}^2}{4I}$ b) $\hat{H} = \frac{\hat{L}}{4I}$ c) $\hat{H} = \frac{\hat{L}^2}{2I}$ d) $\hat{H} = \frac{\hat{L}}{8I}$
- The quantized energy of rigid rotator is
a) $\frac{\hbar^2 l(l+1)}{2I}$ b) $\frac{\hbar l(l+1)}{2I}$ c) $\frac{\hbar^2 l(l+1)}{4I}$ d) $\frac{\hbar^2 l(l+1)}{6I}$

Answers

1	c	2	c	3	a	4	c	5	c
6	c	7	a	8	a	9	c	10	a

References

- ✓ N. Zettili, Quantum Mechanics: Concepts and Applications, John Wiley, 2nd Ed. 2009
- ✓ David J. Griffiths. Introduction to Quantum Mechanics. Pearson Prentice-Hall, second edition, 2005.
- ✓ R. Liboff, Introductory Quantum Mechanics, Addison-Wesley, 4th Ed. 2002.
- ✓ J.S. Townsend, A Modern Approach to Quantum Mechanics, McGraw Hill Book Company, Singapore (1992).
- ✓ R.P. Feynman, R.B. Leighton, and M. Sands. The Feynman Lectures on Physics, volume III. Addison-Wesley, 1965.
- ✓ ABC's of Quantum Mechanics, V. Rydrik, translated by George Yankovsky (1962).
- ✓ R.A. Serway, C.J. Moses and C.A. Moyer, Modern Physics, Brooks Cole, 3rd Ed. 2004.
- ✓ C. Cohen-Tannoudji, B. Diu, F. Laloe, Quantum Mechanics, Volume 1, 1978.
- ✓ J. J. Sakurai, J. Napolitano, Modern Quantum Mechanics. Cambridge University Press 2017.
- ✓ G. Aruldas, Quantum Mechanics, Prentice Hall of India, 2006.